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SOME FACTORS AFFECTING THE PHYSICAL PROPERTIES AND CORROSION RESISTANCE OF 18-8 CHROMIUM-NICKEL STEEL WIRE

By W. H. Wills and J. K. Findley

Abstract

This paper deals with some of the more important factors that have a bearing on the physical properties and corrosion resistance of 18-8 alloy wire. These are based on observations on material as processed through the wire mill and laboratory tests. The advantages and disadvantages of the alloy in the higher carbon range (carbon 0.15-0.20 per cent) are pointed out, also effects of variation of chromium and nickel content.

Methods for stabilizing the alloy, that could be applied particularly to higher carbon material (carbon 0.15-0.20 per cent) are discussed. These consist of (1) heat treatment at 1500 degrees Fahr. for various lengths of time to develop a structural condition resistant to decomposition and (2) the addition of a titanium content. The experiments showed that the latter is more practical as a stabilizer, especially for material going into wire.

Introduction

In a previous paper[1] the essential points that are involved in drawing the 18-8 chromium-nickel alloy steel into wire as well as

[1]W. H. Wills and J. K. Findley, "Manufacture, Properties and Uses of 18-8 Chromium-Nickel Steel Wire," Transactions, American Society for Steel Treating, Vol. XX, p. 97.

A paper presented before the Fifteenth Annual Convention of the society held in Detroit, October 2 to 6, 1933. The authors, W. H. Wills, a member of the society, and J. K. Findley are metallurgists with the Ludlum Steel Co., Dunkirk, N. Y. Manuscript received June 29, 1933.

physical properties were described. Mention was made that the chemical specifications covering material going into wire are:

Carbon	0.07	max.	Silicon	0.20-0.40
Manganese	0.30-0.50		Chromium	17.0-18.0
Phos. and Sul.	0.025	max.	Nickel	9.0-10.0

In general this specification has worked out quite satisfactorily not only as to behavior of the material in process, but also in numerous applications in service. The principal uses for this wire are for screens or wire cloth that go into filters in the paper and chemical industries and for wire rope and springs. The first mentioned application calls for soft wire while the latter two require hard drawn. For the most part the wire is subject to low temperature service involving various types of corrosion, particularly that encountered in aqueous solutions of acids and salts and from electrolytic attack. There are also some cases where it must withstand elevated temperatures that are near or within the range in which carbide precipitation will occur and possibly be in contact with corroding gases.

Extensive work has been done along the line of investigating the so-called carbide precipitation of the chromium-nickel-iron alloys, also ways and means of preventing it.[2] This has included the effect of variation in carbon, chromium, or nickel content, the addition of other elements, the temperature of annealing or heat treatment, and rate of cooling, and the temperature and time of decomposition. According to several investigators a carbon content of 0.02 per cent is the maximum that is completely soluble in the austenite of the 18-8 alloy and with a carbon content above this carbide precipitation follows and the steel is sensitive to intergranular attack. Holding to such a low carbon content is of course impractical commercially and eliminates this method of solving the problem. Practical experience has shown that with carbon up to 0.07 per cent the decomposition range for the alloy is somewhat narrower and the time required to bring it about is much longer than when the carbon content is several points higher, such as 0.15 to 0.20 per cent.

Miller,[3] commenting on the work of several others, brings out that fine grain size and increased chromium content decrease sensi-

[2] V. N. Krivobok, "Further Studies on Chromium-Nickel-Iron and Related Alloys," TRANSACTIONS, American Society for Steel Treating, Vol. XXI, p. 22.

[3] J. L. Miller, "A Study of Intercrystalline Corrosion in Chromium-Nickel Austenitic Steels," Carnegie Scholarship Memoirs, Vol. XXI, p. 128.

tivity to intercrystalline attack to some extent. Also the addition of tungsten, vanadium, copper, aluminum, molybdenum, titanium, or zirconium increases the stability of the austenite matrix and narrows the decomposition range by lowering the upper limit, but none of these methods has been completely successful. His investigation showed that a decomposition temperature of 1200 degrees Fahr. resulted in maximum carbide precipitation and that at 1500 degrees Fahr. maximum agglomeration of the carbides occurred. Also that after homogenizing at 2150 degrees Fahr. and a prolonged anneal (from two to six weeks) at 1500 degrees Fahr. the steel was rendered immune to intercrystalline corrosion. Further experiments showed that after hot working the steel at comparatively low temperatures (1600 down to 1400 degrees Fahr.), a comparatively short annealing period at 1500 degrees Fahr. produced the same effect.

In dealing with the 18-8 alloy in the form of wire there is of course the effect of cold work to be considered in addition to the above mentioned items. In considering some of the factors affecting the properties of 18-8 steel rod and wire it is the authors' purpose to discuss the influence of carbon, and the effect of variation of chromium and nickel contents; and whether the addition of certain other elements and the use of certain heat treatments are practical in order to render the alloy immune from intergranular attack. This information has been gathered from observations and experiments on the material as it is processed through the bar and wire mills supplemented by work in the laboratory.

Effect of Carbon

The primary advantage of using a higher carbon range, such as 0.15 to 0.20 per cent, is, of course, a lower melting cost due to the possibility of utilizing more alloy scrap in the charge and less of the expensive low carbon ferrochromium.

From the standpoint of cold drawing, material in this higher carbon range can be used to better advantage in the production of high tensile rope or spring wire because it requires 5 to 7 per cent less reduction of area by drafting to arrive at a given tensile strength than with the lower carbon (0.07 max.). This means the saving of one roughing pass or the time and die cost of one drawing block. For instance, in making 0.045 hard drawn wire with a guaranteed tensile strength of 255,000 pounds per square inch from the average

run of 0.07 carbon material it is necessary to draw from size 0.120 annealed stock. Using the higher (0.15 to 0.20 per cent) carbon going down to the same size, this tensile strength can be obtained by starting from size 0.100 annealed stock.

Even though the carbon content of regular (carbon 0.07 per cent max.) stock will vary only a few points—practically all heats come in the range 0.05 to 0.07 per cent—and the content of other elements quite similar, the tensile strengths obtained after the rod is given a certain reduction by cold drawing will vary to some ex-

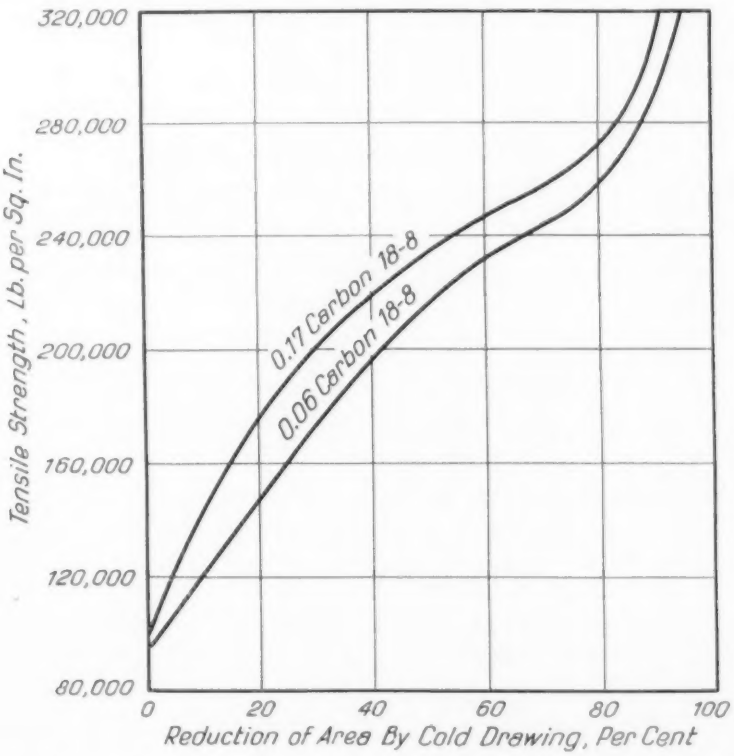


Fig. 1—Curves Showing Relations of Tensile Strengths to Percentage of Drafts on Wire from 0.06 Per Cent Carbon and 0.17 Per Cent Carbon 18-8 Alloys.

tent. This range is something like 10 per cent. Experience in drawing the higher carbon (carbon 0.15-0.20 per cent) rod has shown that this variation is considerably less and the tensile after a given draft will always be at least equal to the highest tensile values obtained with the low carbon stock.

On account of less amount of drafting hard drawn wire of the higher carbon content will be less magnetic than wire of equal tensile strength from low carbon analysis. Medium hard drawn high

carbon wire will be nonmagnetic while when drawn from the low carbon it will be somewhat magnetic. Low magnetic quality is desirable for certain applications in the electrical industry.

The principal disadvantage of this analysis in the higher carbon range (carbon 0.15-0.20 per cent) is that it is more subject to carbide precipitation in the approximate temperature range 1100 to 1700 degrees Fahr. Consequently in process heat treating for softening the wire it has been necessary to go to higher temperatures. Where material with carbon 0.07 per cent maximum is thus treated at 1700 to 1720 degrees Fahr., with a 0.15-0.20 per cent carbon content it is necessary to heat to 1800 to 1850 degrees Fahr. to insure proper structures and freedom from carbide precipitation. This higher temperature means extra time in the heat treating cycle, higher power or fuel consumption, and more deterioration of refractories. Also the scaling loss, particularly as the wire gets down to smaller sizes, is more pronounced and there is more chance for developing a rough surface after pickling. A method designed to overcome this disadvantage by using a special lower temperature heat treatment that brings about carbide agglomeration will be discussed later.

Variation of Chromium and Nickel Content

The lowering of the chromium content alone to less than 16 per cent renders the alloy unworkable from a cold drawing standpoint. It then cannot be treated so as to develop a fully austenitic structure that is ductile at ordinary room temperature. Decreasing the nickel content alone does not improve physical properties and detracts from resistance to corrosion.

One investigator[4] advocates increasing the chromium content over 18 per cent to lessen the tendency toward intergranular attack. However, our experience has not borne this out and there is no improvement in physical properties. Increasing the nickel content to about 12 per cent lessens to some extent the tendency of the metal to cold work, although this is not noticeable on the bend test. It is, however, quite apparent in the production of high tensile wire. For instance with the analysis 17 to 18 per cent chromium and 9 to 10 per cent nickel, a draft of 90 per cent on the wire will produce a tensile of something like 310,000 pounds per square inch. With 17

[4]Shafmeister, Houdremont Notes, Krupp Aktiengesellschaft, "Improved Chromium or Chromium-Nickel Steel Alloys," 1930 British Patent 337,349.

Table I
Tests on Size 0.012 Hard Bright Drawn Wire Run in Connection with Experiments made in Producing High Tensile, Nonmagnetic, Corrosion Resistant Wire

	Analysis					Breaking Load Desired Pounds	Breaking Load Actually Obtained Pounds	Magnetic Permeability (Air = 1.0)	Remarks
	C	Mn	Si	Cr	Ni				
1	0.06	0.40	0.38	17.70	9.60	35.8	36.0	100.0	Tensile OK — Formed well into cable
2	0.10	0.22	0.27	17.16	11.94	35.8	33.5	3.0	Tensile too low — but ductile enough tor flexible cable
3	0.30	0.30	0.24	16.84	11.78	35.8	36.5	3.0	Tensile OK but too hard for flexible cable
4	0.21	0.17	0.31	17.31	12.78	35.8	33.8	6.0	Tensile too low, but ductile enough for flexible cable
5	0.40	0.37	0.30	17.80	8.91	35.8	36.5	over 125.0	Tensile OK — but too hard for flexible cable

to 18 per cent chromium and 11 to 12 per cent nickel a draft of 96 per cent will produce only about 291,000 pounds per square inch tensile strength. Annealed wire of this higher nickel content shows up no better on corrosion tests than that of the regular analysis referred to above even after specimens have been bent to produce the effect of cold working.

Lowering both chromium and nickel to about 16.50 and 8.00 per cent respectively results in wire which has something like 10 per cent higher tensile strength than the regular 17 to 18 per cent chromium and 9 to 10 per cent nickel. However, it will not resist acid attack as well and when annealed has considerably less ductility.

Variation of nickel content as well as carbon has much to do with the magnetic properties after cold working. After a given amount of reduction by cold drawing the magnetic permeability of the wire with higher carbon and nickel content is lower than that of regular analysis. This fact has been the basis of considerable work on wire for extra flexible nonmagnetic corrosion resistant steel cable for aircraft purposes. This wire is required in such sizes as 0.008 up to 0.020 with a tensile strength of 308,000 pounds per square inch and 1.5 maximum magnetic permeability—air being taken as 1. Average wire of the regular specification (carbon 0.07, chromium 17.5, nickel 9.5 per cent) when drawn to this tensile strength shows about 75.0 to 110.0 magnetic permeability. Obviously to bring this figure down to anything like 1.5 it is necessary to have

an alloy whose austenitic phase is not changed so much by the cold working. Two methods suggested themselves for the solution of this problem. (1) Raise the carbon so there is less drafting required to produce the tensile strength. (2) Increase the nickel content to about 12 per cent or a combination of the two. Experiments showed that the analysis (carbon 0.34, chromium 18.0, nickel 9.0 per cent) drawn to the required tensile was too magnetic and too brittle. The composition (carbon 0.10 per cent, chromium 18.0 per cent, nickel 12.0 per cent) would not quite make the desired tensile, but came nearly to the desired result. The results on these tests thus far would indicate that some tensile strength must be sacrificed to obtain the desired magnetic permeability and proper ductility.

Special Additions and Heat Treatments as Means of Stabilization

As stated previously, the 18-8 alloy is subject to decomposition after exposure to moderately elevated temperatures, particularly with higher carbon content (carbon 0.15 to 0.20 per cent). In the course of studying methods of stabilizing the alloy, the effect of additions of a number of other elements has been investigated. A review of the results thus obtained would indicate that the addition of a small titanium content[4, 5] has been the most effective means of stabilization. The addition of about 3 per cent molybdenum to the 18-8 alloy renders it much more resistant to attack in sulphuric acid solutions, although it has little effect on prevention of carbide precipitation at elevated temperatures. Of all the special alloy additions thus far investigated it would appear from a practical standpoint that these two (titanium and molybdenum) are the most useful, although, as just mentioned, each is added for a different purpose.

With the idea of working out a way of rendering the alloy in the higher carbon range (0.15 to 0.20 per cent) more generally suitable for various wire applications it was decided to make a comparison with and without a titanium addition as to physical properties and resistance to intergranular attack following various heat treatments. The tests were made on the material in the form of hot-rolled bars and wire. These were from two 18-8 heats in the higher carbon range (0.15-0.20 per cent) which are designated as A and

[5]E. C. Bain and others, "Prevention of Intergranular Corrosion in Austenitic Stainless Steels," Transactions, American Society for Steel Treating, Vol. XXI, p. 481.

B and two heats of similar analysis with a titanium addition listed as C and D. The analysis of these heats was as follows:

	A	B	C	D
Carbon	0.17	0.20	0.14	0.16
Manganese	0.44	0.81	0.59	0.60
Silicon	0.50	0.58	0.66	0.61
Chromium	18.60	18.06	17.30	16.56
Nickel	8.70	8.62	9.34	9.14
Titanium	..	..	0.66	0.98

Hot-rolled bars of about the same section were obtained from each heat and ¼ inch coils of each were rolled for drawing down into wire.

Tests on Hot-Rolled Bars

The temperature 1200 degrees Fahr. was selected as the one at which decomposition would proceed most rapidly and 1500 degrees Fahr. as the best temperature at which prolonged heating should render the alloy immune to intergranular attack. Samples of the bar stock from each heat were tested after the following:

(1) As-rolled condition.
(2) As-rolled, heated to 1200 degrees Fahr.
(3) Homogenized at 1925 degrees Fahr. and heated to 1200 degrees Fahr.
(4) Homogenized at 1925 degrees Fahr.—Heated to 1500 degrees Fahr.
(5) Homogenized at 1925 degrees Fahr.—Heated to 1500 degrees Fahr. and heated to 1200 degrees Fahr.
(6) As-rolled, heated to 1500 degrees Fahr.
(7) As-rolled, heated to 1500 degrees Fahr.—Reheated to 1200 degrees Fahr.

The periods of time of heating at 1200 and 1500 degrees Fahr. are listed in the accompanying table. Heating of test pieces at this temperature was done in an electric muffle furnace with recording pyrometer.

After the various heat treatments the test pieces were machined to standard 0.505 tensile specimens and pulled on a 100,000 pound universal testing machine. Longitudinal sections from these pieces were taken for micro examination of structure and for corrosion tests in the Strauss solution. The latter were run in boiling 10 per cent $CuSO_4$-10 per cent H_2SO_4 for 200 hours. After pulling, one shoulder of each tensile test was machined to a 60 degree angle and used for the salt spray tests which were run 72 hours in 20 per cent NaCl. The results of the tests on the hot-rolled bar stock are given in Table II. In the "test number" column the letters designate the following:

Table II

Table II

Tests From Hot-Rolled Bars

Test	No.	Heat Treatment	Proof Strength pounds sq.in.	Ultimate Strength pounds sq.in.	Elong. in 4 x dia. %	Red. of Area %	Brinell Hardness No.	Salt Spray 72 hrs. 20%	Strauss Solution Boiling 200 hrs.	Remarks on Microstructure Longitudinal Sections
A	(1)	As-rolled finished approx. 1700° F.	39,000	107,500	45	59	207	Fair	A.	Slightly elongated austenite grains—no slip planes—some carbides at boundaries
A-1	(2)	As-rolled finished approx. 1500° F.	70,000	119,000	39	54	248	Fair	D.	Elongated austenite grains — many boundary carbides
B	(3)	As-rolled finished approx. 1700° F.	45,000	116,000	46	59	207	Fair	H.A.	Austenite grains not developed — carbides mostly in bands along slip planes
C	(4)	As-rolled finished approx. 1700° F.	38,000	97,000	46	62	187	Good	N.A.	Slightly elongated austenite grains — titanium carbides evenly distributed
D	(5)	As-rolled finished approx. 1700° F.	37,250	97,000	47	62	187	Good	N.A.	Slightly elongated austenite grains — titanium carbides evenly distributed
A	(6)	As-rolled (finished 1700° F.) Held 1200° F. 20 hrs.	40,000	102,000	46	59	207	Fair	D.	Slightly elongated austenite grains—many boundary carbides
A-1	(7)	As-rolled (finished 1500° F.) Held 1200° F. 20 hrs.	50,000	110,000	38	52	235	Few pits Fair	D.	Elongated austenite grains —all carbides at boundaries
B	(8)	As-rolled (finished 1700° F.) Held 1200° F. 20 hrs.	46,000	116,000	42	56	207	Fair	A.	Same as (3)
C	(9)	As-rolled (finished 1700° F.) Held 1200° F. 20 hrs.	38,000	98,500	47	60	187	Fair	V.S.A.	Same as (4)
D	(10)	As-rolled (finished 1700° F.) Held 1200° F. 20 hrs.	38,000	98,000	47	60	187	Fair	V.S.A.	Same as (5)
A	(11)	Homogenized 1925° F. Held 1200° F. 3 hrs.	41,000	106,000	39	52	187	Med.	D.	Austenite grains—many small carbides at boundaries
A-1	(12)	Homogenized 1925° F. Held 1200° F. 3 hrs.	41,000	104,000	36	45	187	Med.	D.	Austenite grains—many small carbides at boundaries
B	(13)	Homogenized 1925° F. Held 1200° F. 3 hrs.	56,000	108,000	39	47	196	Med.	D.	Austenite grains — carbides better distributed than (11) and (12)
C	(14)	Homogenized 1925° F. Held 1200° F. 3 hrs.	38,000	100,000	46	62	166	Fair	V.S.A.	Austenite grains—many small titanium carbides in grains
D	(15)	Homogenized 1925° F. Held 1200° F. 3 hrs.	38,000	98,000	46	62	163	Fair	V.S.A.	Austenite grains—many small titanium carbides in grains

A. —Attacked
N.A. —Not Attacked
S.A. —Slightly Attacked
V.S.A.—Very Slightly Attacked
H.A. —Highly Attacked
L.A. —Less Attacked
D. —Decomposed

Table II—Continued

Test	No.	Heat Treatment	Proof Strength pounds sq.in.	Ultimate Strength pounds sq.in.	Elong. in 4 x dia. %	Red. of Area %	Brinell Hardness No.	Salt Spray 72 hrs. 20%	Strauss Solution Boiling 200 hrs.	Remarks on Microstructure Longitudinal Sections
A	(16)	Homogenized 1925° F. Held 1500° F. 34 hrs.	48,000	114,000	38.5	57	187	Fair	S.A.	Austenite grains — carbides mostly at boundaries and somewhat larger than (11)
B	(17)	Homogenized 1925° F. Held 1500° F. 34 hrs.	45,000	107,000	44	60	196	Fair	S.A.	Austenite grains — carbides mostly at boundaries and somewhat larger than (13)
C	(18)	Homogenized 1925° F. Held 1500° F. 34 hrs.	38,750	99,000	48	62	166	Fair	N.A.	Same as (14)
A-1	(19)	Homogenized 1925° F. Held 1500° F. 90 hrs.	46,000	115,000	40	57	187	Fair	S.A.	Apparently same as (16)
B	(20)	Homogenized 1925° F. Held 1500° F. 90 hrs.	48,000	117,000	44	60	187	Fair	S.A.	Apparently same as (17)
C	(21)	Homogenized 1925° F. Held 1500° F. 90 hrs.	38,000	99,500	48	62	166	Fair	N.A.	Apparently same as (18)
A-1	(22)	Homogenized 1925° F. Held 1500° F. 140 hrs.	45,000	114,000	40	58	179	Fair	V.S.A.	Apparently same as (16)
B	(23)	Homogenized 1925° F. Held 1500° F. 140 hrs.	46,000	115,000	46	65	187	Fair	V.S.A.	Apparently same as (17)
A-1	(24)	Homogenized 1925° F. Held 1500° F. 34 hrs. 1200° F. 20 hrs.	45,000	117,000	38	55	187	Fair	A.	Same as (16) except grain boundaries considerably attacked by etching solution
B	(25)	Homogenized 1925° F. Held 1500° F. 34 hrs. 1200° F. 20 hrs.	45,000	115,000	43	57	196	Fair	L.A. than 24	Same as (17) except grain boundaries considerably attacked by etching solution
C	(26)	Homogenized 1925° F. Held 1500° F. 34 hrs. 1200° F. 20 hrs.	39,000	98,000	48	62	166	Fair	N.A.	Same as (18)
A-1	(27)	Homogenized 1925° F. Held 1500° F. 140 hrs. 1200° F. 20 hrs.	44,000	115,000	40	56	179	Fair	S.A.	Same as (24)
B		Homogenized 1925° F. Held 1500° F. 140 hrs. 1200° F. 20 hrs.	47,000	118,000	45	65	179	Fair	S.A.	Same as (25)
A-1	(28)	As-rolled—held 1500° F. 34 hrs.	50,000	115,500	38.5	57	212	Fair	A.	Elongated austenite grains — mostly at boundaries — slightly larger than in (2)
B	(29)	As-rolled—held 1500° F. 34 hrs.	48,000	116,000	42	57	207	Fair	S.A.	Same as (3)

A. —Attacked S.A. —Slightly Attacked H.A. —Highly Attacked D. —Decomposed
N.A. —Not Attacked V.S.A.—Very Slightly Attacked L.A. —Less Attacked

Table II—Continued

A. —Attacked
N.A. —Not Attacked
S.A. —Slightly Attacked
V.S.A.—Very Slightly Attacked
H.A. —Highly Attacked
L.A. —Less Attacked
D. —Decomposed

Table II—Continued

Test No.		Heat Treatment	Proof Strength pounds sq.in.	Ultimate Strength pounds sq.in.	Elong. in 4 x dia. %	Red. of Area %	Brinell Hardness No.	Salt Spray Corrosion 72 hrs. 20%	Strauss Solution 10% $CuSO_4$ 10% H_2SO_4 Boiling 200 hrs.	Remarks on Microstructure Longitudinal Sections
C	(30)	As-rolled—held 1500° F. 34 hrs.	39,000	98,000	45	62	166	Fair	N.A.	Same as (4)
D	(31)	As-rolled—held 1500° F. 34 hrs.	40,000	100,000	45	62	179	Fair	N.A.	Same as (5)
A-1	(32)	As-rolled—held 1500° F. 48 hrs.	50,000	116,000	38.5	57	212	Fair	S.A.	Same as (28)
B	(33)	As-rolled—held 1500° F. 48 hrs.	47,500	116,000	41	57	207	Fair	S.A.	Same as (29)
C	(34)	As-rolled—held 1500° F. 48 hrs.	38,000	99,000	46	60	179	Fair	V.S.A.	Same as (30)
A-1	(35)	As-rolled—held 1500° F. 72 hrs.	48,000	115,000	40	56	207	Fair	V.S.A.	Carbides all near boundary and slightly larger than (28)
B	(36)	As-rolled—held 1500° F. 72 hrs.	46,000	115,500	44	58	207	Fair	N.A.	Same as (29) but carbides slightly larger
A-1	(37)	As-rolled—held 1500° F. 34 hrs. 1200° F. 20 hrs.	49,000	116,000	38	55	207	Few pits	D.	Same as (28) except grain boundaries considerably attacked
B	(38)	As-rolled—held 1500° F. 34 hrs.	45,000	116,000	42	57	207	Few pits	D.	Same as (29) except etch attack in vicinity of carbides
C	(39)	As-rolled—held 1500° F. 34 hrs.	38,000	99,000	45	60	179	Fair	V.S.A.	Same as (30)
D	(40)	As-rolled—held 1500° F. 34 hrs.	38,000	100,000	46	62	179	Fair	V.S.A.	Same as (31)
A-1	(41)	As-rolled—held 1500° F. 48 hrs. 1200° F. 20 hrs.	50,000	115,000	38	56	212	Fair	A.	Same as (37)
B	(42)	As-rolled—held 1500° F. 48 hrs.	48,000	116,000	40	58	207	Fair	S.A.	Same as (38)
A-1	(43)	As-rolled—held 1500° F. 72 hrs. 1200° F. 20 hrs.	48,500	116,000	40	57	207	Fair	S.A.	Same as (35) except grain boundaries slightly more etched out
B	(44)	As-rolled—held 1500° F. 72 hrs.	47,500	115,750	43	57	207	Fair	S.A.	Same as (36) except slight etch attack in vicinity of carbides

A. —Attacked
N.A. —Not Attacked
S.A. —Slightly Attacked
V.S.A.—Very Slightly Attacked
H.A. —Highly Attacked
L.A. —Less Attacked
D. —Decomposed

A	1″ sq. from Heat A
A-1	1″ rd. from Heat A
B	¾″ rd. from Heat B
C	1″ rd. from Heat C
D	1″ rd. from Heat D

Tests on Wire

The ¼-inch hot-rolled coils from the four heats designated as A, B, C and D respectively were annealed for cold drawing by heating to 1900 degrees Fahr. and water quenching. Parts of coils A and B were drawn to size 0.100 wire taking the usual drafts and with process anneals at 1820 degrees Fahr. for softening. These were again divided into two lots that were held at 1500 degrees Fahr. for different lengths of time. Part of each of these was next drawn to 0.050 while the remainder was held first at the decomposition temperature—1200 degrees Fahr. for 20 hours and then drawn to 0.050. Samples of the 0.100 wire annealed and after holding at 1500 degrees Fahr. were tested for tensile and for corrosion resistance in the Strauss solution. Similar tests were run on the 0.050 as drawn from 0.100 (not annealed) and on the same after holding at 1200 degrees Fahr. for short and long periods. This group of tests was to determine the effect of the 1500 degrees Fahr treatment on hard drawn wire. Samples of 0.050 annealed wire were treated at 1500 degrees Fahr. followed by heating to 1200 degrees Fahr. and drawn to 0.025. At this size tensile and corrosion tests were run on the wire hard drawn and bright annealed.

In the foregoing tests the 1500 degrees Fahr. treatments were all run on annealed wire. The next group of tests were run on wire in a strained or medium hard drawn condition. The 0.100 wire was annealed at 1820 degrees Fahr. and cold drawn to 0.072 in which condition it was held at 1500 degrees Fahr. for 36 hours and further drawn to 0.050. It was then tested in the same way as drawn and after holding at 1200 degrees Fahr. for 30 minutes.

The next group of tests (from Coil A) was run on high tensile wire to investigate the effect of short and long time heating at the decomposition temperature—1200 degrees Fahr. Part of Coil A was drawn according to regular practice to 0.055 and annealed at 1800 degrees Fahr. The 0.055 was drawn to 0.016 with no anneals. The tensile and corrosion tests were run after holding 15 minutes and 24 hours at 1200 degrees Fahr. See Table III.

Coils C and D (titanium heats) were each divided into two

Table III

Wire From Coil A Processing and Tests

¼-inch coils from Heat A, Water quenched from 1900° F. } Tensile Strength—97,000 lbs. per sq.in. Elongation in 6 inches—56% Strauss Solution—N.A.

Drawn to Size 0.150 — Tensile Strength—250,000 lbs. per sq.in. Strauss Solution—N.A.

Annealed 1820° F. — Tensile Strength—100,000 lbs. per sq.in. Elongation in 6 inches—54% Strauss Solution—N.A.

Drawn to Size 0.100 — Tensile Strength—247,000 lbs. per sq.in. Strauss Solution—V.S.A.

Annealed 1820° F. — Tensile Strength—102,000 lbs. per sq.in. Elongation in 6 inches—48%—Strauss Solution—N.A.

PART 1

Held 1500° F. 48 hrs. } Tensile 101,000 Elongation 45% Strausss Sol. D.

Part held 1200° F. for 20 hrs. Tensile—95,000 Elongation 38 Strauss Sol. D.

Part Drawn to 0.050 Tensile—230,000 Strauss Sol. A.

Drawn to 0.050 Tensile—229,000 Strauss Sol. A.

PART 3

Held 1500° F. 90 hrs. Tensile 99,000 Elongation 46% Strauss Sol. A.

Part held 1200° F. 20 hrs. Tensile 99,000 Elongation 41% Strauss Sol. D.

Part Drawn to 0.050 Tensile—227,000 Strauss Sol. S.A.

Drawn to size 0.050 Tensile 227,000 Strauss Sol. V.S.A.

PART 4

Cold drawn to 0.072 Tensile 202,000 Strauss Sol. N.A.

Held 1500° F. 36 hrs. Tensile 140,000 Strauss Sol. N.A.

Drawn to 0.050 Tensile 214,000 Strauss Sol. V.S.A.

Held 30 min. 1200° F. Tensile 214,000 Strauss Sol. V.S.A.

Part 2 Drawn to 0.050

PART 2

Size 0.050 Annealed 1820° F.—Tensile 107,000 Elongation 51%—Strauss Sol. N.A.

PART 2 (a)

Held 1500° F. 48 hrs.—Tensile 107,000 Elong. 44% Strauss Sol. S.A.

Drawn to size 0.025—Tensile 240,000 Strauss Sol. S.A.

Part held 1200° F. 3 min. Tensile 200,000 Strauss Sol. D.

Part Bright Annealed 2100° F. in Hydrogen Atmosphere Tensile 105,000 Elongation 39% Strauss Sol. N.A.

PART 2 (c)

Held 1500° F.—48 hrs. } Tensile 102,000 1200° F.—20 hrs. } Elongation 40% Strauss Sol. D.

Drawn to 0.025—Tensile 236,000 Strauss Sol. A.

Bright Annealed 2100° F. Tensile 100,000 Elongation 39% Strauss Sol. N.A.

PART 2 (b)

Drawn to 0.016 without intermediate anneals—Tensile 300,000 Strauss Sol. N.A.

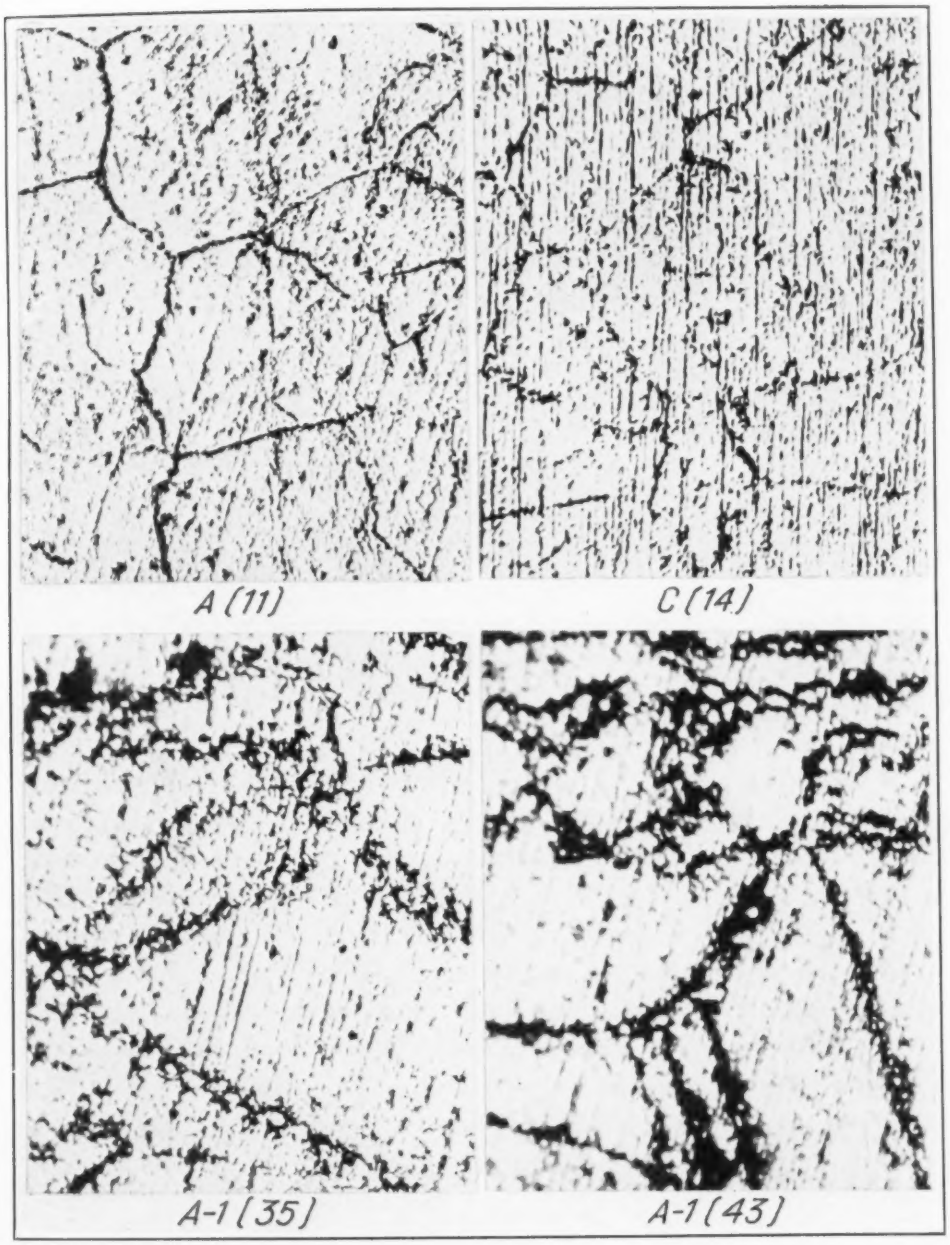
Held 1200° F.—3 min.—Tensile 200,000—Strauss Sol. A.

Held 1200° F.—2 hrs.—Tensile 185,000—Strauss Sol. V.S.A.

Table IV

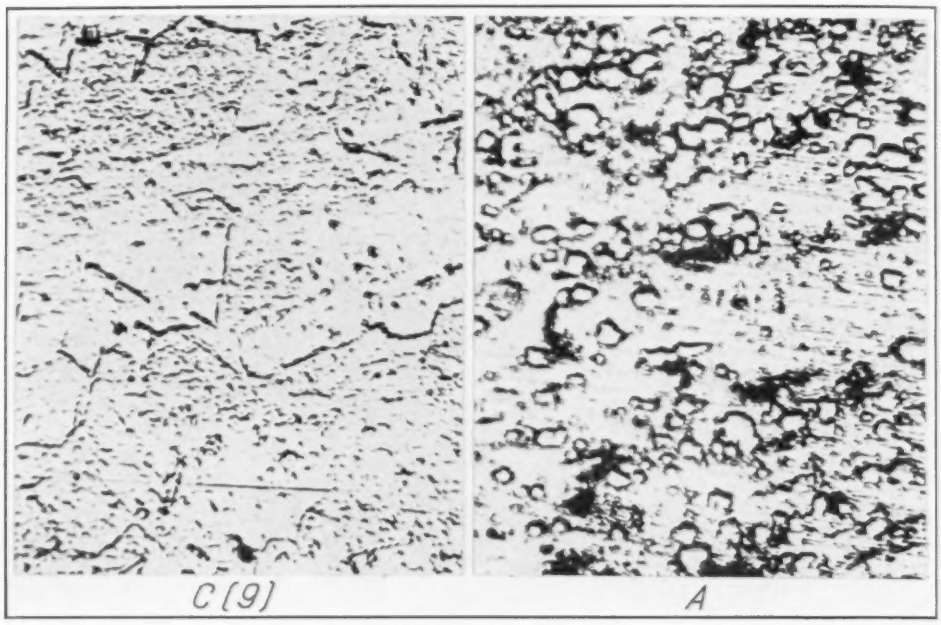
Wire From Coils C and A Processing and Tests
¼-Inch Hot-Rolled Coils Water-Quenched From 1900 Degrees Fahr.

Coil C Tensile—92,000 Elongation—57 Strauss Sol.—N.A.		Coil A Tensile—97,000 Elongation—56 Strauss Sol.—N.A.	
Divided in 2 Parts		Divided in 2 Parts	
Part 1	Part 2	Part 1	Part 2
Drawn to size 0.150 Tensile—244,000 Strauss Sol.—N.A.	Drawn to size 0.150 Tensile—244,000 Strauss Sol.—N.A.	Drawn to size 0.150 Tensile—250,000 Strauss Sol.—N.A.	Drawn to size 0.150 Tensile—250,000 Strauss Sol.—N.A.
Annealed 1820° F. —water Tensile—96,000 Elongation—52 Strauss Sol.—N.A.	Annealed 1720° F. —water Tensile—96,000 Elongation—54 Strauss Sol.—N.A.	Annealed 1820° F. —water Tensile—100,000 Elongation—54 Strauss Sol.—N.A.	Annealed 1720° F. —water Tensile—102,000 Elongation—54 Strauss Sol.—N.A.
Drawn to 0.090 Tensile—245,000 Strauss Sol.—V.S.A.	Drawn to 0.090 Tensile—248,000 Strauss Sol.—N.A.	Drawn to 0.090 Tensile—256,000 Strauss Sol.—V.S.A.	Drawn to 0.090 Tensile—250,000 Strauss Sol.—A.
Annealed 1820° F. —water Tensile—97,000 Elongation—52 Strauss Sol.—N.A.	Annealed 1720° F. —water Tensile—99,000 Elongation—55 Strauss Sol.—V.S.A.	Annealed 1820° F. —water Tensile—100,000 Elongation—50 Strauss Sol.—N.A.	Annealed 1720° F. —water Tensile—106,000 Elongation—49 Strauss Sol.—V.S.A.
Drawn to 0.050 Tensile—250,000 Strauss Sol.—N.A.	Drawn to 0.050 Tensile—248,000 Strauss Sol.—V.S.A.	Drawn to 0.050 Tensile—260,000 Strauss Sol.—V.S.A.	Drawn to 0.050 Tensile—255,000 Strauss Sol.—S.A.
Annealed 1820° F. —water Tensile—100,000 Elongation—46 Strauss Sol.—N.A.	Annealed 1720° F. —water Tensile—102,000 Elongation—48 Strauss Sol.—N.A.	Annealed 1820° F. —water Tensile—105,000 Elongation—45 Strauss Sol.—N.A.	Annealed 1720° F. —water Tensile—112,000 Elongation—40 Strauss Sol.—V.S.A.
Drawn to 0.024 Tensile—254,000 Strauss Sol.—N.A.	Drawn to 0.024 Tensile—256,000 Strauss Sol.—N.A.	Drawn to 0.024 Tensile—264,000 Strauss Sol.—V.S.A.	Drawn to 0.024 Tensile—260,000 Strauss Sol.—S.A.
Annealed 1820° F. —water Tensile—100,000 Elongation—40 Strauss Sol.—N.A.	Annealed 1720° F. —water Tensile—101,000 Elongation—40 Strauss Sol.—N.A.	Annealed 1820° F. Tensile—104,000 Elongation—42 Strauss Sol.—N.A.	Annealed 1720° F. Tensile—115,000 Elongation—38 Strauss Sol.—S.A.
Drawn to 0.010 Tensile—265,000 Strauss Sol.—N. A.	Drawn to 0.010 Tensile—265,000 Strauss Sol.—V.S.A.	Drawn to 0.010 Tensile—272,000 Strauss Sol.—N.A.	Drawn to 0.010 Tensile—268,000 Strauss Sol.—A.
Bright Annealed 2100° F. Hydrogen Atmosphere	Bright Annealed 2100° F. Hydrogen Atmosphere	Bright Annealed 2100° F. Hydrogen Atmosphere	Bright Annealed 2100° F. Hydrogen Atmosphere
Tensile—105,000 Elongation—44 Strauss Sol.—N.A.	Tensile—104,000 Elongation—54 Strauss Sol.—N.A.	Tensile—106,000 Elongation—52 Strauss Sol.—N.A.	Tensile—105,000 Elongation—56 Strauss Sol.—V.S.A.
Small Amount Heated to 1200° F. for 3 minutes Tensile—194,000 Strauss Sol.—N.A.		Small Amount Heated to 1200° F. for 3 minutes Tensile—187,000 Strauss Sol.—S.A.	



A (11) Homogenized 1925 Degrees Fahr. Held 3 Hours at 1200 Degrees Fahr.
C (14) Homogenized 1925 Degrees Fahr. Held 3 Hours at 1200 Degrees Fahr.
A-1 (35) As-Rolled. Held 72 Hours at 1500 Degrees Fahr.
A-1 (43) As-Rolled. Held 72 Hours at 1500 Degrees Fahr. Reheated 20 Hours at 1200 Degrees Fahr. All Photomicrographs × 2000.

groups—one part of each drawn down to fine wire using 1720 degrees Fahr. process anneals (Same as used on low carbon 18-8)



C (9) As-Rolled. Finished at 1700 Degrees Fahr. Reheated 20 Hours at 1200 Degrees Fahr. × 2000.
A Cold Drawn from 0.100 to 0.072. Annealed. Held 36 Hours at 1500 Degrees Fahr. × 2400.

while with the other part, 1820 degrees Fahr. process anneals were used. (Same as used on high carbon material.) Samples of these lots were tested and compared for tensile and corrosion resisting properties. Part of Coil C was drawn to 0.016 high tensile wire similar to the portion from Coil A and tested after long and short time at the decomposition temperature—1200 degrees Fahr. The procedure followed with these wire tests will probably be made clearer by reference to Tables II and III which give the results of the physical and corrosion tests. As Coil B showed physicals very close to A and D resembled C results are given in the table for coils A and C only. See Table IV.

Conclusion

The results obtained from the tests on the bar stock as well as the wire from the 18-8 alloy in the higher carbon range (carbon 0.15-0.20 per cent) show that short time heating at 1500 degrees Fahr. (up to 48 hours) does not improve physicals and only slightly improves resistance to corrosion. Somewhat longer time at 1500 degrees Fahr. (72 to 140 hours) producing a structure with fairly

large agglomerated carbides, does not improve physicals and somewhat improves resistance to attack after holding at the decomposition temperature, 1200 degrees Fahr. From a practical standpoint the benefits from the long treatment at 1500 degrees Fahr. would hardly be worth the extra cost. In the case of the wire the scale thus produced while not heavy is of the type that clings tenaciously and increases the cost of pickling materially.

The material from the heats with a titanium addition in the as-rolled condition also as-rolled and heated to the decomposition temperature, 1200 degrees Fahr., was not changed as to physicals and showed much better resistance to attack than the straight 18-8. Very short time heating (1 hour) of the latter at 1200 degrees Fahr. has a decidedly detrimental effect on physicals and corrosion resistance, whereas, with titanium content the effect is small in comparison.

Holding the titanium material at 1500 degrees Fahr. for periods up to 90 hours had very little effect on physicals and resistance to corrosion. There appeared to be no tendency of the carbides to agglomerate, indicating the stability of the titanium carbide constituent. In the case of the titanium alloy the 1500 degrees Fahr. treatment was tried merely for comparison with the straight 18-8 alloy.

The titanium 18-8 wire drawn with process anneals at 1720 degrees Fahr. showed up satisfactorily as to physicals and corrosion resistance, although the physicals were slightly under those of the straight 18-8 (carbon 0.15-0.20 per cent) put through with process anneals at 1820 degrees Fahr.

Of the two methods for stabilizing the 18-8 alloy, namely, heat treatment at 1500 degrees Fahr. and the use of a titanium addition, the latter is decidedly the more practical and efficient. The principal disadvantage of titanium is the high loss in making the addition to the bath or charge in the melting operation, also the difficulty in getting a uniform distribution through the metal.

Acknowledgments

The authors wish to express their thanks to F. B. Lounsberry, vice president of Ludlum Steel Company, for suggestions and permission to present the data given in this paper. They also are grateful for the co-operation of W. P. Schnabel, in charge of the Fine Wire Department, in running numerous experiments and tests on the wire.

DISCUSSION

PETER R. KOSTING:[1] This is a most interesting paper, showing the effect of cold working and annealing on the phenomenon attributed to carbide precipitation. I should like to ask for a description of the method used in evaluating the degree of attack for both types of specimens so that a better estimate can be made of the differentiation between "D" : "A" : "S.A." : "V.S.A." : and "N.A."

Author's Reply[2]

In reply to Mr. Kosting's question, I might state that we did not make any weight determinations on these corrosion tests. The ratings were made merely from the appearance of the polished specimens. The corrosion test specimens of bar stock were polished as for a micro specimen, and visual examination was made after immersion in the Strauss solution. Specimens noted as "D" (Decomposed) were in such a condition that the surface layers would simply crumble away. "A" (Attacked) referred to a condition where the surface was almost completely covered with copper; "S.A." (Slightly Attacked) partially covered with copper and surface roughened as examined at 25 diameter magnification; "V.S.A." (Very Slightly Attacked) no copper deposited on surface and surface slightly roughened when examined same way. "N.A." (Not Attacked) referred to perfectly smooth surface as observed at same magnification.

In the case of the wire, samples were examined under a low power binocular microscope and compared before and after immersion in the Strauss Solution.

[1]Watertown Arsenal, Watertown, Mass.

[2]Reply made by W. H. Wills.

INVESTIGATION OF THE TREATMENT OF STEEL FOR PERMANENT MAGNETS—PART II

By R. L. Dowdell

Abstract

This paper gives the results of aging miscellaneous steels when treated for permanent magnets. Results show that tempering at 100 degrees Cent. for 12 hours, followed by tempering in the magnetized state until about 5 per cent of magnetic induction is lost, followed by sacrificing 5 per cent more by a reversed demagnetizing field, gave the greatest stability of any of the treatments used.

This treatment indicates that both hardening and magnetic strains should be partially removed in order to stabilize permanent magnets regardless of their composition. The several tables included give the treatment and aging characteristics over a period of about ten years.

Introduction

ABOUT ten years ago Part I of this investigation was presented before the fifth annual convention of this society in Pittsburgh, October 8-12, 1923.[1] It is the purpose of the present paper to present data showing the aging characteristics of miscellaneous steels of the general alloy and permanent magnet types. As there has been relatively little published research on the aging of hardened steels in the magnetized state, it is believed that the results offered may be of value in stabilizing magnetic circuits subject to high leakage.

Experimental Work

The chemical composition of the steels is given in Table I, and it will be noted from this table that many steels are included which are not classed as permanent magnet steels.

All of the following data given on the aging characteristics of these steels were obtained from straight bar magnets ten inches in

[1]R. L. Dowdell, "Investigation of the Treatment of Steel for Permanent Magnets," Transactions, American Society for Steel Treating, Vol. V, 1924, p. 27.

A paper presented before the Fifteenth Annual Convention of the society held in Detroit, October 2 to 6, 1933. The author is a member of the society and is professor of metallography, University of Minnesota, Minneapolis, Minn. Manuscript received July 3, 1933.

Table I
Chemical Composition of Steels

No.	Per Cent C	Mn	Si	P	S	Cr	W	Ni	Co	V	Mo
					Tungsten Steels						
68	0.53	0.36	0.40	0.017	0.007	0.57	5.17	....	.....	....	....
69	0.67	0.56	0.29	0.013	0.018	0.18	5.07	....	.....	....	....
73	0.67	0.61	0.31	0.014	0.007	0.20	5.43	....	.....	....	....
74	0.61	0.38	0.25	0.022	0.027	none	5.31	....	.....	....	....
88	0.76	0.61	0.56	0.022	0.011	0.41	5.08	....	.....	....	....
					Chromium Steels						
67	0.72	0.56	0.35	0.011	0.014	2.17	0.19	....	.....	....	....
70	0.97	0.74	0.33	0.031	0.005	2.87	....	....	.....	....	....
71	0.80	0.56	0.30	0.013	0.002	2.16	....	....	.....	....	....
					Carbon Steels						
51	0.70	0.63	0.17	0.028	0.033	....	....	....	.....	....	....
54	0.74	0.57	0.20	0.016	0.007	....	....	....	.....	....	....
75	0.98	0.65	0.11	0.033	0.018	....	....	....	.....	....	....
76	1.18	0.56	0.11	0.020	0.021	....	....	....	.....	....	....
104	0.76	0.84	0.29	0.015	0.025	....	....	....	.....	....	....
105	0.76	0.52	0.28	.....	0.011	....	....	....	.....	....	....
106	0.54	1.28	0.27	0.021	0.032	....	....	....	.....	....	....
					Miscellaneous and Special Steels						
15	0.35	0.45	0.23	0.019	0.008	....	....	5.03	.....	....	....
18	0.11	0.22	0.10	0.021	0.001	15.70	....	....	.....	....	....
37	0.41	0.85	0.14	0.013	0.024	0.89	....	2.59	.....	....	....
81	0.43	0.63	0.26	0.013	0.012	....	....	3.54	.....	....	....
84	0.39	0.90	0.24	0.020	Tr	0.51	....	1.37	.....	....	....
97	0.34	0.40	0.11	0.002	0.034	0.77	....	....	.....	....	0.72
98	0.50	0.70	0.16	0.002	0.021	1.05	....	....	.....	0.22	....
99	0.86	0.13	0.16	0.015	0.041	9.31	....	....	13.66	....	1.24

length by 3/8 inch in diameter. The bars were all water-quenched (tap water, 5-10 degrees Cent.) after machining from 3/4 inch round bars previously annealed or normalized. Hardening was done from a lead pot in most cases after holding at the hardening temperatures shown for 15 minutes. Hardness was determined with the Rockwell machine on the "C" scale and all tabulated readings were taken at the middle of the bars. The hardness at the ends was usually several points higher than at the middle portion.

It is realized that the bars have a rather high demagnetizing effect or flux leakage and that with different dimensions and different heat treatments many of the steels might have shown different losses in magnetic induction.

The apparatus for magnetic testing is discussed in Part I. Briefly, the magnetic induction (B_{rem}) was determined by dropping the magnet through a stationary test coil and noting the deflection of a ballistic galvanometer calibrated frequently by a mutual inductance.[2]

[2]Smith, "Theory and Practice of Electrical Measurements"; Purdue University, 1909, p. 241.

Table II

Natural Aging of Permanent Magnets

Treatment No. 1, Magnetized After Hardening; Stored in Vertical Position

Steel and Bar No.	Ac_3 °C.	Qu Temp. °C.	R "C" Hard.	(−Hc) oe	After Hardening	When Stored	After 40 Days	After 171 Days	After 375 Days	Magnetic Induction—Brem After 497 Days	After 642 Days	After 740 Days	After 775 Days	After 1000 Days	After 2465 Days	After 3562 Days	% Loss During Aging
51-1	750	760	61	65.0	9160	9160	8797	8556	8317	7959	7743	7356	7277	7050	6870	5563	39.2
54-1	735	745	65	69.3	8560	8560	8200	7902	7635	7305	7108	6690	6604	6380	6050	5530	35.4
76-1	800	810	64	81.0	8157	8157	8042	7535	7237	6947	6767	6326	6257	5850	5720	5280	35.0
68-1	760	770	57	58.2	10413	10413	10028	9891	9562	9175	8982	8535	8435	8085	8030	7500	27.9
69-1	760	770	61	63.0	10868	10868	10568	10460	10079	9664	9500	9061	8970	8420	8380	7780	28.4
73-1	750	760	48	54.0	7369	7369	7104	6816	6799	6572	6367	6014	5930	3280	3285	3080	58.2
74-1	750	760	41	57.3	9240	9240	8641	8508	8330	7980	7698	7360	7210	6756	6980	6500	35.3
74-2	750	850	58	65.0	10011	10011	9530	9420	8891	8777	8507	8096	8010	7035	8180	7720	35.0
74-3	750	950	63	72.2	10755	10755	10545	10443	10079	9684	9445	9061	8885	8300	8180	7720	28.2
74-4	750	600‡	50	63.1	9189	9189	8925	8726	8448	8124	7876	7481	7400	6640	6260	5580	39.3
67-1	765	775	58	56.1	10456	10456	10114	9704	9250	9068	8846	1402	8300	6815	8090	7110	32.0
70-1	765	775	63	65.0	10450	10450	10200	10022	9636	9317	9167	1687	8525	7815	7680	7170	31.4
71-1	765	775	61	56.6	10509	10509	10255	10460	9803	9625	9309	1877	8830	7080	8370	7750	26.2
15-1	680	690	53	47.0	7979	7979	7609	7368	7174	6964	6798	1358	6319	5910	5940	5390	32.4
81-1	705	715	50	43.3	6202	6202	5820	5664	5452	5298	5160	2835	4795	3905	3867	3600	41.8
84-1	721	731	41	36.0	5569	5569	5292	5077	4821	4787	4633	4347	4328	3270	3875	3345	39.9
37-1	715	725	54	44.5	8540	8540	8186	7908	7561	7419	7148	6815	6752	5510	6519	5935	30.5
														Average per cent loss.....			35.1

Steel and Bar No.	Ac_3 °C.	Qu Temp. °C.	R "C" Hard.	(−Hc) oe	After Hardening	When Stored	After 40 Days	After 58 Days	After 145 Days	Magnetic Induction—Brem After 290 Days	After 323 Days	After 2465 Days	After 3562 Days	% Loss During Aging
98-1 Ac?	867	878	53	51.0	37.5	8721	8584	8507	8294	7737	7680	7158	6345	27.2
97-1	785	795	48	44.5	31.0	7356	7129	7039	6847	6367	6274	4950	4588	37.6
99-1	840	850	50	122.8	103.8	8766	8766	8715	8553	8065	7980	....	....	....
98-4	763	773	53	50.0	36.7	8613	8454	8335	8104	7601	7445	6370	5955	30.8
97-5	785	875	50	44.5	31.7	7567	7362	7220	7055	6566	6418	6200	5745	23.0
97-6	785	950	48	43.2	31.0	7359	7180	7084	6921	6418	6271	5995	5505	25.2
99-4	840	900	52	126.1	107.1	8834	8897	8787	8687	8152	8042	7875	7380	16.5
99-5	840	950	48	136.5	122.7	8613	8675	8582	8439	7934	7875	7590	7100	17.5
												Average per cent loss.....		25.4

‡Heated to 1150 degrees Cent. (2100 degrees Fahr.) air-cooled to 600 degrees Cent. (1112 degrees Fahr.).

Table III

Artificial and Natural Aging of Permanent Magnets

Treatment No. 5, Magnetized After Hardening; Remagnetized and Tempered at 100 Degrees Cent. in Air Until Approximately 5 Per Cent of B_{rem} was Lost; Aged in Vertical Position.

Steel and Bar No.	Ac_3 °C.	Qu Temp. °C.	R "C" Hard.	Held at 100° C. for	Magnetic Induction—B_{rem} After Hardening	After Temper	After Sacrifice	When Stored	After 3 Days	After 19 Days	After 140 Days	After 175 Days	After 1845 Days	After 2935 Days	% Loss After Storing
51-360	750	760	66	40 min.	8182	7754	....	7754	....	7305	7229	7046	....	5970	23.0
54-250	735	770	66	40 min.	8286	7472	....	7472	7471	7128	6989	6803	6530	6000	19.7
69-250	760	795	63	40 min.	10156	9423	....	9423	9381	8973	8832	8622	8505	7865	16.5
88-160	761	771	65	40 min.	10242	9687	....	9687	9664	9241	9049	8834	8800	8070	16.7
67-30	765	800	50	40 min.	10238	9574	....	9574	9542	9155	8964	8800	8650	7990	16.6
15-250	680	715	52	25 min.	7630	6898	....	6898	6897	6572	6401	6298	6095	5565	19.3
81-250	705	715	55	25 min.	7669	6776	....	6776	6733	6396	6246	6140	5800	5300	21.8
37-360	715	725	51	25 min.	8277	7663	....	7663	....	7220	7148	6955	6485	5905	22.7
98-20	867	878	55	25 min.	8632	8061	....	8061	7985	7637	7426	7341	7035	6320	27.0
99-20	840	850	51	45 hrs.	8947	8613	....	8613	....	8221	8220	8035	....	7385	14.3
														Average per cent loss.....	19.8

Treatment No. 6, Magnetized After Hardening; Remagnetized and Tempered at 100 Degrees Cent. in Air Until Approximately 5 Per Cent of B_{rem} was Lost; Bar Partly Demagnetized in Reversed Field Until Approximately 5 Per Cent More of B_{rem} was Lost; Aged in Vertical Position

54-360	735	770	65	47 min.	7919	7587	7257	7257	7211	6876	6697	6550	5915	5400	25.6
69-360	760	770	55	20 min.	11017	9653	9162	9162	9120	8721	8618	8462	8245	7682	16.3
88-250	761	796	62	20 min.	10335	9815	9380	9380	9289	8843	8786	8618	8165	7660	18.3
67-460	765	775	62	15 min.	9355	8935	8457	8457	8414	7948	7941	7705	6810	6380	24.6
15-360	680	715	46	20 min.	7348	6741	6422	6422	6388	6064	5929	5835	5640	5275	17.8
81-360	705	715	45	15 min.	6924	6435	6140	6140	6127	5774	5642	5545	5150	4760	22.5
98-30	867	878	47	20 min.	8636	8040	7666	7666	7616	7263	7103	6997	6735	6275	18.1
99-30	840	850	50	45 hrs.	9088	8715	8300	8300	....	....	8243	8130	....	7580	8.9
														Average per cent loss.....	18.9

Table IV

Artificial and Natural Aging of Permanent Magnets

Treatment No. 7, Magnetized After Hardening; Demagnetized and Tempered at 100 Degrees Cent. for 12 Hours and Remagnetized. Magnetized Bar Tempered at 100 Degrees Cent. in Air Until Approximately 5 Per Cent of B_{rem} was Lost; Aged in Vertical Position

Steel and Bar No.	Ac_3 °C.	Qu Temp. °C.	R "C" Hard.	Held at 100° C. for	After Hard-ening	After Demag. Temp.	After Mag. Temp.	After Sacri-fice	When Stored	Magnetic Induction—B_{rem} After 3 Days	After 19 Days	After 140 Days	After 175 Days	After 1845 Days	After 2935 Days	% Loss After Storing
76-250	800	810	65	50 min.	7413	7480	7192	....	7192	7169	6794	6748	6630	6470	5650	21.4
73-250	750	785	49	25 min.	8313	8402	7964	....	7964	7958	7516	7498	7350	7320	6840	14.2
70-250	765	800	61	75 min.	9409	9383	9016	....	9016	9016	8631	8555	8390	8265	7360	18.3
18-150	825	860	34	25 min.	5823	6306	5600	....	5600	5594	5294	5272	5152	5040	4685	16.3
84-250	721	756	37	25 min.	5640	5790	5475	....	5475	5418	5102	5105	4990	4975	4610	15.8
97-20	785	820	50	25 min.	7650	7388	7019	....	7019	6998	6621	6586	6450	6040	5605	20.1
													Average per cent loss.....			17.7

Table V

Artificial and Natural Aging of Permanent Magnets

Treatment	Steel and bar No.	Ac_3 °C.	Qu Temp. °C.	R "C" Hard	Magnetic Induction—B_{rem} After Hardening	After *	After †	After ‡	After 10 Quenches	When Stored	After 15 days	After 84 days	After 125 days	After 136 days	After 171 days	After 1845 days	After 2935 days	% Loss after storing
No. 9	51-250	750	785	64	8128	....	....	7720	(Q 7X)	7720	7343	....	....	7222	7087	....	5788	25.0
No. 9	37-250	715	725	51	8118	....	....	7734	(Q 5X)	7734	7282	....	....	7222	6951	....	5959	22.9
No. 10	105-1	740	750	63	7710	7610	....	....	7222	7222	....	7176	7090	....	....	6425	5230	27.8
No. 10	105-2	740	750	64	7535	7336	....	....	6953	6953	....	6907	6803	....	....	6105	4692	32.5
No. 11	105-3	740	750	60	7427	....	7392	....	6774	6774	....	6725	6619	....	....	5460	4200	38.0
No. 11	105-4	740	750	61	7595	....	7546	....	7072	7072	....	7023	6920	....	....	6640	4775	32.4
No. 12	105-5	740	750	60	7925	....	....	....	7072	7072	....	7023	6871	....	....	6475	4965	29.7
No. 13	105-11	740	820	60	6936	6936	....	....	....	6493	....	6470	6348	....	....	5485	4510	30.5
No. 13	105-12	740	820	62	6686	6638	....	....	....	6306	....	6306	6202	....	....	5370	4512	28.4
No. 14	105-13	740	820	61	6941	....	6969	....	....	6603	....	6506	6425	....	....	5290	4675	29.2
No. 14	105-14	740	820	61	6742	....	6765	....	....	6115	....	6068	5980	....	....	5045	4445	27.3
																	Average per cent loss....	29.0

Treatments: Magnetized After Hardening.

*Bar Demagnetized and Tempered at 100 Degrees Cent. for 10 Hours and Remagnetized.

†Bar Demagnetized and Tempered at 100 Degrees Cent. for 20 Hours and Remagnetized.

‡Magnetized Bar Repeatedly Quenched from Water Bath at 100 Degrees Cent., in Ice Water at 0 Degrees Cent., After Holding 5 Minutes at Each Until Approximately 5 Per Cent of B_{rem} was Lost.

Magnetized Bar Given 10 Quenches from Water at 100 Degrees Cent. to Ice Water at 0 Degrees Cent., Holding 5 Minutes at Each Temperature.

Aged in Vertical Position.

Table VI

Artificial and Natural Aging of Permanent Magnets

Treatment No. 15, magnetized after hardening; magnetized bar quenched from 20°C. in carbon dioxide snow at −57°C., after being held in the snow until approximately 5% of B_{rem} was lost. Aged in vertical position.

Steel and Bar No.	Ac_3 ° C.	Qu Temp. ° C.	R "C" Hard	Magnetic Induction—B_{rem} After Hardening	After Temper.	After sacrifice	When stored	After 11 days	After 133 days	After 167 days	Held in snow for	After 1845 days	After 2935 days	% Loss after storing
51-40	750	785	65	8348	....	7936	7936	7572	7462	7330	90 min.	6415	5858	26.1
54-40	735	745	55	7771	....	7334	7334	6885	6759	6660	20 min.	6060	5430	26.0
69-40	760	795	63	7891	....	9682	9682	9304	9096	8949	125 min.	8170	7620	21.3
71-250	765	775	63	9769	....	9334	9334	8933	8789	8665	115 min.	8370	7530	19.3
18-30	825	860	33	5535	....	5277	5277	5044	4974	4935	40 min.	4225	2910	44.8
15-40	680	715	52	7397	....	7027	7027	6646	6392	6315	40 min.	5880	5415	22.9
81-40	705	715	48	5622	....	5329	5329	5022	4861	4770	35 min.	3420	3225	39.4
											Average per cent loss			28.5
Treatment No. 16, same as No. 15 except that the bars were demagnetized and tempered at 100°C. for 12 hours; then remagnetized before the carbon dioxide quenches.														
76-40	800	810	64	7659	7505	7401	7401	6884	6782	6735	65 min.	6450	5980	19.2
73-40	750	760	29	5065	5086	4810	4810	4516	4449	4416	40 min.	2920	2705	43.7
70-40	765	800	58	9471	9280	9019	9019	8656	8562	8436	247 min.	7020	6555	27.3
84-40	721	731	31	5526	5514	5224	5224	4920	4849	6735	23 min.	2782	2595	50.3
37-40	715	725	51	8453	8232	7959	7959	7543	7436	7328	60 min.	7070	6570	17.4
											Average per cent loss			31.6
Treatment No. 17, magnetized after hardening; demagnetized and tempered at 100°C. and remagnetized; quenched 5 times in CO_2 snow from water at 100°C. and held 5 min. each.								81 da.	115 days					
105-6	740	750	61	7595	7447	7123	7123	7072	6970	Temp. 10 hrs.		6185	5765	19.0
105-7	740	750	61	7163	7163	6785	6785	6640	6585	Temp. 20 hrs.		6350	5805	14.4
105-9	740	750	64	7688	7542	7163	7163	7118	7008	Temp. 20 hrs.		6470	6020	16.0
105-10	740	750	61	7481	....	6806	6806	6617	6510	Not tempered		5995	5500	19.2
											Average per cent loss			17.1

The results of aging the miscellaneous steels after hardening and magnetizing only are shown in Table II, together with the hardness and quenching temperatures. In this particular group aging was carried out for about ten years, while for the magnets treated in various ways before aging the tests have been conducted only about eight years (Tables III, IV, V, and VI). The magnets were stored by suspending them vertically with string from the ceiling of a large room.

Those interested in the choice and design of permanent magnets for special purposes should consult the papers by Evershed,[3] Watson,[4] and Sanford,[5] because this paper does not enter into that phase of the subject. Other important papers on theory and practice with permanent magnet steels are listed in the references of the National Metals Handbook, 1933, p. 884.

Summary

Tables III to VI inclusive show the complete aging characteristics of the miscellaneous steels when used as permanent magnets.

The group of magnets having the lowest percentage loss (14.8) in magnetic induction for an eight-year period was given treatment 8 which consists of:

1. Magnetize after hardening.
2. Demagnetized and tempered at 100 degrees Cent. for 12 hours.
3. Remagnetized and tempered at 100 degrees Cent. until 5 per cent magnetic induction lost.
4. Sacrifice of 5 per cent magnetic induction in reversed field.

The above treatment would indicate that when magnetic stability is desired it is necessary to relieve partially both hardening and magnetic strains.

The group of magnets having the highest percentage loss (35.1)

[3]S. Evershed, "Permanent Magnets in Theory and Practice," *Journal,* Institute Electrical Engineers, Vol. 58, 1920, p. 780.

[4]E. A. Watson, "Magnetos for Ignition Purposes in Internal Combustion Engines," *Journal,* Institute Electrical Engineers, Vol. 59, 1921, p. 145.

"Permanent Magnets and the Relation of Their Properties to the Constitution of Magnet Steel," *Journal,* Institute Electrical Engineers, Vol. 61, 1923, p. 641.

[5]R. L. Sanford, "Some Principles Governing the Choice and Utilization of Permanent Magnet Steels," *Science Paper,* Bureau of Standards No. 567, Vol. 22, 1927, p. 557.

in magnetic induction for a ten-year period was given treatment 1 which consisted simply of magnetizing after hardening.

It also appears that individual magnets from all the different treatments lose their induction, in nearly all cases, in the same sequence as found with the various groups.

It is interesting to note that the percentage decrease in induction on aging after the different treatments is nearly a constant for a period of about eight years if the sacrificed induction is taken into account.

Acknowledgment

The writer kindly acknowledges the valuable assistance of Miss C. H. Green, assistant in the Department of Metallography, University of Minnesota, for aid in this work.

DISCUSSION

Written Discussion: By John A. Mathews, vice president, Crucible Steel Co. of America, New York City.

We need more papers of the kind presented by Dr. Dowdell; that is, representing the effect of long-time experience with materials. These papers are relatively few. The classic work of Barus and Strouhal dealt with high carbon tool steels which were first studied in 1885 and kept under observation for a period of a great many years. I do not have before me the various papers on the subject but as I recall it there were some conclusions reached which were for a long time accepted as gospel in metallurgical work. The first, as I recall it, was that steel when tempered to a given temperature attains stability practically as soon as the full tempering temperature is reached. The second conclusion was that after tempering at a given temperature no further effects might be expected by re-tempering at any lower temperature. These ideas became pretty well fixed in our earlier metallurgical beliefs. They may be approximately true for high carbon drill rods which were the subject of the investigation, but they are certainly not true of alloy steels which occupy so much of our attention today. E. C. Bain has recently given us some information upon the sluggishness of the reactions of certain steels. In certain steels the reactions are very fast and in some other steels they are very slow. The recent use of corrosion and scale-resisting steels for long periods at elevated temperatures has brought out interesting information in regard to long time changes in physical properties.

The writer had considerable difficulty in persuading a customer to remove two apparently good parts of a chemical apparatus after two years of service for the purpose of studying what had been going on. The application was an entirely new one and it seemed as though such a study might be made to advantage. The length of time which it takes certain changes to become complete

leads me to doubt how valuable the results of creep tests may be which are only conducted for a period of a few hundred hours. I believe there is great uncertainty in translating these results into terms of creep for 10,000 or 100,000 hours.

In connection with Dr. Dowdell's work one might come to the conclusion that the inherent magnetic properties as determined by the permeameter have little to do with the use of the steels as permanent magnets. There seems to be no relation between the falling off in residual magnetism with time and the original coercive force shown in Table II. This is because Dr. Dowdell, fortunately or unfortunately, used very long slender rods for the purpose of his tests. The residual density as shown in the original permeameter tests seems to be the controlling factor rather than the coercive force. If the author would take some of these bars and gradually cut down the length, say one inch at a time, he will eventually reach a ratio of length to cross section where coercive force rather than initial residual induction is the more important factor. At the time his original paper was presented 10 years ago we were making experiments along somewhat similar lines. These included chromium, tungsten and cobalt magnets. When all the steels were arranged in the order of their coercive forces, which varied between 59 and 182, there appeared to be no relation between them and the bar magnet flux of the bars which were 12 inches long by ¼ inch cross section. For example, a chromium magnet steel with a coercive force of 62 gave a somewhat higher bar magnet flux than a cobalt magnet with a coercive of 182. When these bars were cut down to about one-half their original length, the steel with a coercive of 182 showed twice the flux of the chromium magnet steel and when the magnets were again cut in two the cobalt magnet steel had over three times the flux of the chromium magnet steel. A freshly charged magnet always seems to me to represent a condition analogous to supersaturation. A portion of its magnetism may be "precipitated" very readily by the effect of time, impact and vibration and by slight thermal changes. Again a freshly charged magnet might be compared with a bushel measure of wheat piled up to its maximum capacity. A slight vibration will cause much of the wheat to spill over the edge until a condition is reached where the grain is level with the edge of the container. After this has happened considerable stability is attained. In the case of permanent magnets, the makers of instruments have long recognized this condition and have resorted to various artificial aging methods to reduce the initial flux to a place where the balance of the flux may be depended upon, otherwise the calibration of electrical measuring instruments would be very undependable. In the case of certain cobalt magnet steels capable of giving a rather wide range of properties, according to the kind of heat treatment employed, we hardened a series of bars in various ways so that in the end we had a range of coercive forces from 120 to 194—all representing the same analysis. If we consider the highest coercive force as representing the best hardened bar, then it was noted that the bar magnet flux corresponding to the best treatment was very much below that of certain of the bars which might be considered as having been improperly hardened. Again, it was noted in this series that after standing for a month and being retested on the permeameter, there was a considerable loss in coercive force, particularly in all those steels which were improperly hardened,

but that in the two samples representing good hardening the coercive force was practically unchanged. This loss in coercive force sometimes amounted to as much as 7 to 9 points. The residual magnetism in the permeameter test showed an increase in practically every bar in the series during the first month. I do not think that any of Dr. Dowdell's results indicate an increase in residual density during the first short period after hardening but this, it should be recalled, was probably because all his tests except the original ones, were made upon slender bar magnets rather than by the permeameter method in which the steels are tested in a practically closed magnetic circuit. In the case of the last series of tests which the writer has discussed, I am inclined to think that the changes affecting the coercive force may illustrate the sluggishness of reactions and that decreases in the coercive force after one month's time were for the most part the result of a completion of the austenite-martensite transformation and the same would account for the gain in residual density due to the creation of more alpha iron by the decomposition of the austenite. It was noted that when the change in coercive was relatively small the increase in residual was also small and that when the change in coercive was large the increase in residual was also large.

Written Discussion: By W. H. Wills, Ludlum Steel Co., Dunkirk, N. Y.

The data obtained by this research should be of interest to manufacturers of permanent magnets for comparison with results which they get following their methods of heat treating and aging.

The necessity of partially relieving both hardening and magnetic strains to obtain magnetic stability is in line with practice followed in the making of permanent magnets. Older methods called for rather long periods of aging before final testing. This is in contrast to the treatments now used that produce the effect of aging in a comparatively short time.

It was noticed that the Rockwell C hardness of the carbon, also of the tungsten, and chromium magnet steels as quenched varied considerably which may be from underheating in hardening. If it was desired to develop full hardness corresponding to a fully martensitic structure, a hardness something like 63 to 66 would be expected as quenched, and this is desired to develop a high coercive force (H_c). Low hardness values are shown in Table II tungsten magnet steels 73-1 and 74-1 where values of coercive force (H_c) are on the low side, and the residual magnetism B_{rem} is considerably under 10,000. However, the results would indicate that this does not affect the aging loss and the high loss 58.2 per cent shown by sample 73-1 is difficult to account for.

The cobalt magnet steel No. 99 shows up well as to aging loss even when simply magnetized after hardening.

Author's Closure

The author regrets that he was not present for the discussion of this paper but nevertheless is glad to read the written discussions by authorities in the field of magnet steels, namely, Dr. J. A. Mathews and Mr. W. H. Wills.

In reply to the discussion by Mr. Wills, I must admit that in some cases the hardness of the magnets was not too high and as Mr. Wills suggested would account for the low values of B_{rem} and H_c. It appears that quenching $\frac{3}{8}$ inch

bars from only 10 degrees Cent. above the upper critical is not high enough to bring out the best combination of magnetic properties and that with this small margin there were irregularities which probably were responsible for the decreased hardness and high aging loss of tungsten bar No. 73-1.

Dr. Mathews has pointed out the fact that with low magnetic ratios (1/d) a high value of coercive force is of far more importance than in the case of the slender bars used in this work. I am particularly interested in the experiments conducted by Dr. Mathews wherein he found that aging for one month showed a loss in coercive force and a gain in residual magnetism when determined by permeameter tests. These changes indicated strongly that the gamma to alpha transformation had taken place and check in principle with my results which were reported in Part I, TRANSACTIONS, American Society for Steel Treating, Vol. V, 1924, p. 51, Fig. 13, where similar magnets (3/8 inch diameter by 10 inches length) were tempered cumulatively at 50 and 100 degrees Cent. for one hour each and then remagnetized. In nearly all cases there was an increase in B_{rem} which reached a maximum at 100 degrees Cent. and then rapidly decreased as the tempering temperature increased above 100 degrees Cent. The results given in Table IV of Part II also show increases in B_{rem} after tempering for 12 hours. It is believed that the majority of the bars which were magnetized after quenching and stored would also have increased in B_{rem} on room temperature aging had they been remagnetized and tested, but this series (Table II) was stored immediately after magnetizing and was not remagnetized to check this point. Even in the case of slender magnet bars in open circuit testing it appears that the gamma to alpha transformation can be detected and shows the sluggishness of the gamma to alpha transformations in special steels.

The suggestions that a freshly charged magnet is analogous to supersaturation in physical metallurgy is indeed a good one and metallurgists as well as farmers must agree that the heaping bushel of wheat may be considered analogous to a charged magnet, especially at this time.

In conclusion I wish to thank Dr. Mathews and Mr. Wills for their important discussion.

A STUDY OF THE EFFECT OF WATER VAPOR ON THE SURFACE DECARBURIZATION OF STEEL BY HYDROGEN WITH CERTAIN DEVELOPMENTS IN GAS PURIFICATION

By C. R. Austin

Abstract

Much experimental work has been devoted to a study of the decarburization of steel by hydrogen and the literature is extensive and to some extent contradictory.

The present paper sets forth data obtained under experimental conditions more refined than hitherto and outlines the method adopted for the preparation of "pure hydrogen."

It is demonstrated by chemical and metallographic analyses that the pure gas has a definite but extremely limited decarburizing power at 800 degrees Cent. on eutectoid steels, and that as the water vapor content of moist hydrogen gas is increased (except in very low concentration) the decarburizing power of the gas is also profoundly increased.

In very low concentration (10 milligrams water vapor per cubic foot of hydrogen) the presence of water vapor appears to reduce further the limited decarburizing power of the dry gas.

The observations recorded should have commercial value in the application of "dry hydrogen" to bright anneal of high carbon steels concomitant with freedom from surface decarburization.

THE literature on the effect of a hydrogen atmosphere on the surface decarburization of steels during annealing is extensive and to some extent contradictory. In the bright annealing of low carbon steels use is frequently made of hydrogen gas, or of some commercial gas containing hydrogen in the elementary or combined form, as the medium for a controlled atmosphere. Some bright finished steel manufacturers have recently reported success on annealing high carbon steels in hydrogen bearing gases and consider

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that such bright annealing in dissociated ammonia gas (which contains 75 per cent hydrogen) can be accomplished with little or no loss of carbon from the surface of the bar or sheet.

It has generally been considered that hydrogen gas is a strong decarburizing agent for steel. A good bibliography of previous work is given by Jominy,[1] where that writer states that pure dry hydrogen is reported to cause decarburization by Ledebur,[2] Herwig,[3] Austin,[4] Sykes,[5] Johansson and Von Seth,[6] and others. It is reported not to cause decarburization Wüst and Geiger,[7] Wüst and Sudhoff,[8] and by Emmons.[9] It is reported to cause practically no decarburization at 850 degrees Cent. (1560 degrees Fahr.) or below in three hours' time by Schulz and Hülsbruck and to decarburize very mildly above this temperature. There is a similar lack of agreement regarding the influence of pure dry nitrogen.

The apparent contradictions with respect to pure dry hydrogen are probably chiefly due to one or more of the following factors:

(1) There is considerable difference in interpretation in what is meant by a "pure dry gas."

(2) The time factor in experimentation has varied considerably with different authors, and it would seem that in some cases the time of experimentation has been too brief to permit drawing definite conclusions.

(3) The method of determining whether decarburization has occurred illustrates considerable difference in the refinement of technique, and hence in the conclusions that would be thereby drawn.

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[1]W. E. Jominy, *Engineering Research Bulletin* No. 18, University of Michigan, March, 1931.

[2]A. Ledebur, *Stahl und Eisen*, Vol. 6, 1886, p. 373.

[3]W. Herwig, *Stahl und Eisen*, Vol. 33, 1913, p. 1721.

[4]C. R. Austin, *Journal*, Iron and Steel Institute, Vol. 105, 1922, p. 93.

[5]W. P. Sykes, TRANSACTIONS, American Society for Steel Treating, Vol. 12, 1927, p. 737.

[6]A. Johansson and R. Von Seth, *Journal*, Iron and Steel Institute, Vol. 114, 1926, p. 295.

[7]J. Wüst and G. Geiger, *Stahl und Eisen*, Vol. 25, 1905, p. 1134.

[8]F. Wüst and E. Sudhoff, *Metallurgie*, Vol. 7, 1910, p. 261.

[9]J. Emmons, American Institute of Mining Engineers, Vol. 50, 1914, p. 405.

Some of the more recent results published were those of Johansson and Von Seth. This important contribution to the subject considers the decarburization of thin steel cuttings in a current of pure hydrogen, but does not include surface effects on bar stock in this gas. The cuttings were heated for a period of 16 hours at different temperatures in the pure gas and the change in carbon content determined by chemical analysis. The results indicate that decarburization is apparent at about 600 degrees Cent. (1110 degrees Fahr.) and then increases very quickly at about 650 to 700 degrees Cent. (1200-1290 degrees Fahr.), reaching a maximum at 950 degrees Cent. (1740 degrees Fahr.). The authors also record the slighter disposition of chromium steels to decarburize in comparison with pure carbon steels.

Present Investigation

The present paper considers the development of a gas purification train whereby all so-called traces of water vapor and free oxygen could be removed from the gas system. It discusses methods of determining and checking gas purity, and of making predetermined quantitative water vapor additions to the purified gas. Data are given illustrating the decarburizing effect of pure dry hydrogen and of pure hydrogen with known water vapor additions, on a plain carbon steel and on a steel containing 1.5 per cent chromium.

Preliminary Work

It is considered desirable to make reference to some preliminary experiments which throw light on the surface decarburization effects of moist and dried dissociated ammonia gas and of ordinary tank and dried tank hydrogen. The steel used in these preliminary experiments was 1⅛ inch nominal diameter bar stock of S.A.E. 52100 specification, turned down to 1 inch in order to remove any surface decarburization effects occurring during course of manufacture.

The conditions of treatment, including time, temperature, and atmosphere, with remarks from metallographic examinations, are given briefly in Table I. A 2 inch diameter silica tube was used for the tests with a constant gas flow of 2 cubic feet per hour.

The first seven experiments demonstrated that water vapor speeded up the decarburization rate to a remarkable degree, but it

Table I

Treatment of Preliminary Series of Tests on S.A.E. 52100 with Observations From Metallographic Examination

Experiment	Sample No.	Time Hours	Treatment Temp. Degrees Cent.	Atmosphere	Remarks
1	A	8	775	Moist diss. NH_3	Decarburized ferrite band 50 units wide.
2	B	1	775	Moist diss. NH_3	Peripheral ferrite band about 13 units wide.
3	C	0.62	775	Moist diss. NH_3	5 to 10 units irregular free ferrite periphery.
4	D	0.65	775	Moist hydrogen	About 15 units wide ferrite band.
5	E	0.6	775	Tank hydrogen	No microscopic evidence of decarburization.
6	E	1.5	775	Tank hydrogen	No evidence of decarburization.
7	E	7.5	775	Tank hydrogen	Still no evidence of decarburization.
8	F	0.5	775	Dry diss. NH_3	No decarburization.
9	F	7.5	775	Dry diss. NH_3	Still no evident decarburization.
10	F	26	775	Dry diss. NH_3	Possibly slight decrease in peripheral C content.
11	F	50	775	Dry diss. NH_3	Recorded definite signs of decarburization.
12	G	50	775	Dry diss. NH_3	Slight decarburization. See Table II.
13	H	50	775	Dry diss. NH_3	Slight decarburization. See Table II.
14	I	21	950	Dry diss. NH_3	Slight decarburization.
15	I	40	950	Dry diss. NH_3	Slight decarburization.
16	I	86	950	Dry diss. NH_3	Definite slight reduction in peripheral carbon.
17	J	45	950	Dry diss. NH_3	Analytical data. See Table II.

was considered of importance to determine how long the anneal must be continued in dry gas before definite visible signs of surface decarburization could be discovered under the microscope. The dissociated ammonia was used as being the source of purest hydrogen excepting nitrogen and water vapor. The gas was dried by passing over calcium chloride followed by activated alumina. The latter appears to be one of the most powerful dehydrating agents available.

The desiccating power of activated alumina has been discussed by Barnitt, Derr and Scripture.[10] In testing this desiccating power the dissociated ammonia gas was passed successively through a gas meter, sulphuric acid towers, a calcium chloride and two activated alumina towers, and finally through a liquid air trap containing glass-wool packing. 32 cubic feet of gas were passed in 29.5 hours. The water collected by the liquid air trap was determined by passing 1 cubic

[10]Alumina in a new form as a laboratory desiccant. *Industrial and Engineering Chemistry*, Oct. 15, 1930, p. 355.

Table II

Table Showing Carbon Content of Successive Peripheral Layers Cut From a 1-Inch Bar of S.A.E. 52100 After the Prescribed Treatment

Experiment 12 Treated in Dried Diss. Ammonia at 775 Degrees Cent. for 50 hrs.	Experiment 13 Treated in Dried Diss. Ammonia at 775 Degrees Cent. for 50 hrs. Using Liquid Air Trap		Experiment 17 Treated in Dried Diss. Ammonia at 950 Degrees Cent. for 45 hrs.	
5 mil cut	*3 mil cut*	*10 mil cut*		
Per cent carbon	Per cent carbon	Per cent carbon	Per cent carbon	
1st 0.91	1st 0.90	1st 0.96	1st 0.84	*3 mil cut*
2nd 0.95	2nd 0.95	2nd 0.99	2nd 0.84	
3rd 1.00	3rd 0.99	3rd 1.01	3rd 0.87	
4th 1.01	4th 1.01	4th 1.05	4th 0.86	
5th 1.03	5th 1.03	5th 1.06	5th 0.86	
	6th 1.05	6th 1.07		
	7th 1.03	7th 1.08	1st 0.86	*10 mil cut*
	8th 1.06	8th 1.04	2nd 0.89	
	9th 1.07	9th 1.06	3rd 0.90	
	10th 1.04	10th 1.07	4th 0.91	
			5th 0.99	
Average carbon content of bar stock 0.95 per cent	Average carbon content of sample given as 1.07 per cent		Same steel as in Experiment 10	

foot of dry warm air first through the trap after removing the cooler and then through a phosphorus pentoxide tube. If it be assumed that the liquid air trap removes all traces of water allowed to pass by the alumina, then the 8.3 milligrams increase in weight of the pentoxide tube indicated that after passing over activated alumina the gas contained only 0.26 milligrams water per cubic foot. A later check on the efficiency of this drier gave the figure 0.11 milligrams water per cubic foot gas.

The dry gas tests on decarburization show the reaction to be extremely slow at 775 degrees Cent. This temperature was used on account of the fact that it approximates to that used in the industrial annealing of high carbon steels where a relatively soft easily machinable spheroidized structure is desired. However, it was thought that the problem might be more readily studied by elevating the temperature of experimentation.

At 950 degrees Cent. (1740 degrees Fahr.) a marked increase in rate of decarburization was observed and the penetration effect was much deeper. In the analytical data found in Table II certain irregularities in the change in carbon content from surface toward center are evident. The analysis found in successive peripheral turnings taken from a bar "as received" after first removing any commercially decarburized layer, are given in Table III.

An examination of these data suggests that any carbon content

Table III

Carbon Analyses Obtained from Successive Layers of S.A.E. 52100 in the "as received" State, After First Removing a 1/16 Inch Skin from the Hot-Rolled Bar

Cut	Successive 3 mil cuts per cent carbon	Successive 10 mil cuts per cent carbon
1st	1.08	1.08
2nd	1.05	1.08
3d	1.09	1.06
4th	1.10	1.05
5th	1.07	1.05
6th	1.10	1.06
7th	1.12	1.05
8th	1.07	
9th	1.07	
10th	1.07	

differences of magnitude less than 0.05 per cent do not have any real significance in our study of decarburization gradients, since it is possible that such differences may be due to heterogeneity in the steel plus errors in chemical analysis.

Discussion of Preliminary Results

The data already presented indicate that there is unquestionably a marked difference in the surface decarburizing power of dry and moist hydrogen. As previously mentioned, it is believed that much of the variance found in the literature is due to the interpretation of what is meant by a "dry gas." Thus in Experiment 13 (Table I) the dissociated ammonia was dried under very carefully regulated experimental conditions and surface decarburization was reduced to a very limited amount.

The question naturally arises, if the water vapor had been "completely removed" would the surface decarburization have been completely prevented?

In considering the purification of gases by various means one of the greatest problems is to find some method of analysis or some index which will effectively demonstrate the degree of success in the attempted purification. During experimental work on gas-metal reactions it was observed that pure iron is extremely sensitive to the formation of oxide films in certain temperature ranges when only minute traces of free oxygen are present in the surrounding atmosphere. An even greater sensitivity to free oxygen and/or water vapor was exhibited by stainless steel. Thus the gas which was purified by the method already outlined, and which would chemically be regarded as pure hydrogen plus nitrogen (Experiments 8

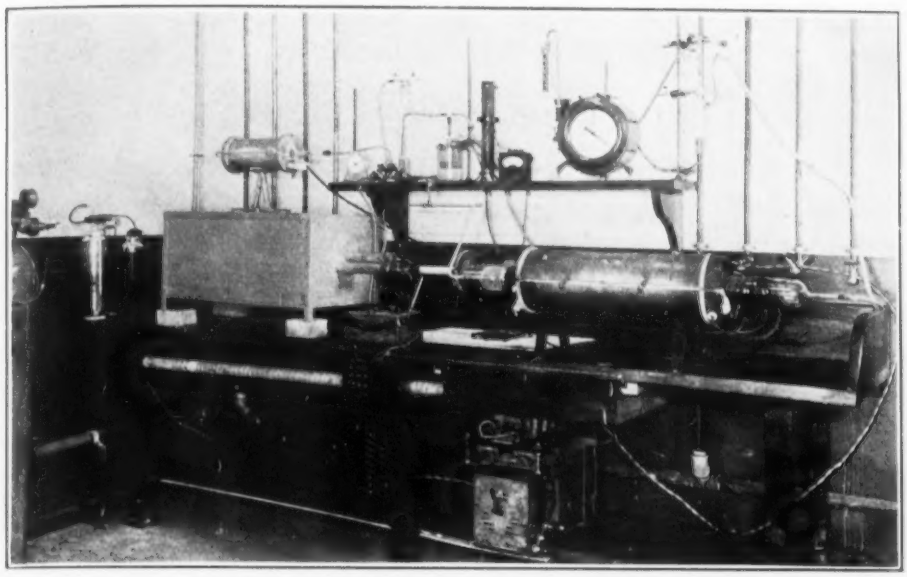

Fig. 1—Photograph of Apparatus Used in this Investigation.

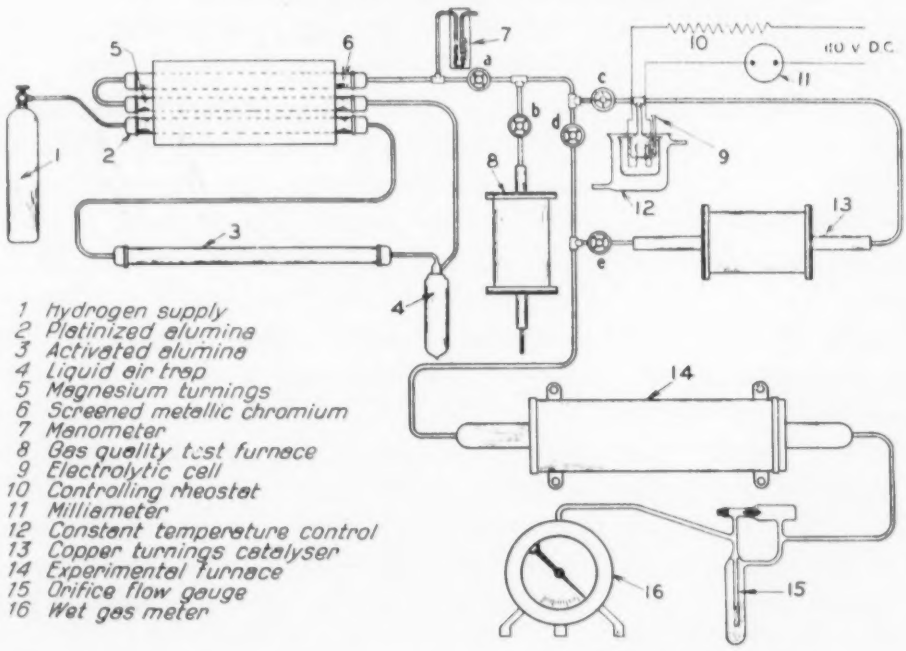

Fig. 2—Schematic Diagram of Apparatus Used in this Investigation.

to 17), rapidly oxidized a stainless steel strip which was subject to an anneal in the gas. This extreme sensitivity of the nickel-chromium-iron alloy, to the production of oxide films showing interference colors, was used in the subsequent series of experiments to

indicate when "pure gas" had been obtained for experimental purposes.

Developments in Gas Purification

It will not be possible to go through the various steps in the development of apparatus which was considered capable of purifying hydrogen gas, so attention will be focused on the final unit evolved and on the attention to details necessary for successful operation. Throughout the following experimental part of the investigation tank hydrogen was used as the source of gas supply in order to eliminate any possible modifying effects due to the presence of nitrogen.

A general picture of the apparatus used in the gas purification along with the annealing and gas testing furnace is shown in Fig. 1. The purpose of each piece of apparatus along with its relative position in the general assembly will be more readily understood by reference to the diagrammatic sketch (Fig. 2).

The hydrogen from the tank (1) is first passed through platinized alumina (2) at 625 degrees Cent. (1155 degrees Fahr.) in order to effect combination of any free oxygen. The water formed is removed by the activated alumina (3) followed by a liquid air trap (4). The gas at this stage is chemically pure hydrogen. This so-called pure gas then passes over magnesium turnings (5) and finally over screened metallic chromium (6) heated to 625-630 degrees Cent. (1155-1165 degrees Fahr.). Any possible traces of oxygen, both free and combined as water vapor, along with any nitrogen are thereby removed. The manometer (7) serves to indicate the pressure built up in the purification system and suitably arranged needle valves permit the gas to be passed through the gas quality test furnace (8) and/or through the annealing furnace (14). The calibrated flow meter (15) serves to indicate the flow rate and the meter (16) gives the total amount of gas used during an experiment. The remaining part of the apparatus will be discussed in a later section.

Considerable care is essential in building up and assembling the units in order to obtain consistently successful results. The tubes (2, 5 and 6) located in one furnace were made of Allegheny metal. Each tube had a 12-inch metal spacer at each end so that the parts of the tubes outside the furnace did not contain any of the purification reagent, while the other portion was completely

filled in such manner as to prevent channeling. All seven connections were sealed with a red lead and glycerine mixture, and metal connectors with copper tubing rendered the system gas tight.

Tube 3 containing the ¼-inch granular activated alumina was wound with nichrome over the entire length so that on applying 110 volts the temperature of the alumina was raised to about 170 degrees Cent. for reactivation. During experimentation a back pressure of about 10 inches of mercury (4-5 pounds) was maintained by throttling valve (a). This was to combat diffusion of air into the system through small leaks, as despite every precaution leaks occasionally did make their appearance as evidenced by the gas quality tests. After reconditioning any of the tubes the train was run for some time with the application of heat to pipe ends, screw caps, etc. to assist in removing adsorbed gases. From time to time the gas quality was tested by passing the gas over heated stainless steel in furnace 8. Finally when the gas was "good" a 60-minute anneal of the stainless steel strip at about 700 degrees Cent. (1290 degrees Fahr.) resulted in no evidence of tarnishing. This test was taken as an index of really pure gas, and the annealing experiment conducted in furnace 14, was started. The gas was again tested at or near the conclusion of the experiment.

Effect of Water Vapor on Hydrogen Decarburization

In order to have two commercial steels for comparison the following two alloys were selected.

Table IV
Analysis of Alloys Used in the Investigation

Material	C	Mn	P	S	Si	Ni	Cr
S.A.E. 52100	1.07	0.310	0.013	0.014	0.22	0.08	1.42
P. 2209	1.11	0.29	0.022	0.031	0.21	...	...

It was considered that the chromium steel would show a pronounced less disposition to decarburize.*

The specimens were turned from 1⅛ inch hot-rolled bar down to 1-inch round. This eliminated any decarburized skin and presented an oxide free bright metallic surface. The bars were 7 inches long, and contained the original centers for future turning in the lathe to provide concentric peripheral turnings. The specimens

*This has been discussed previously by the writer in a contribution to a paper by E. D. Campbell, J. S. Ross, and W. L. Fink, *Journal*, Iron and Steel Institute, 1923, Vol. II, p. 186.

Table V

Analytical Data Taken From the Plain Carbon Steel Samples (P2209) After Treating as Indicated

Sample	P0	P1	P2	P3	P4	P5	P10	P12
Annealing Treatment	As received	55 hrs. 800° C	55 hrs. 750° C	55 hrs. 750° C	55 hrs. 800° C	55 hrs. 800° C	55 hrs. 800° C	55 hrs. 800° C
Annealing Atmosphere		Pure dry hydrogen	H_2 sat. water	H_2 +10 mg. water /cu.ft.	H_2 +50 mg. water /cu.ft.	H_2 +150 mg. water /cu.ft.	H_2 sat. water	H_2+ 10 mg. water /cu.ft.
Sfce. appearance after anneal	Bright mirror like	Light grey	Blue grey	Light grey	Light grey	Silvery grey	Grey, some bluing	Light grey
Location of sample	Per Cent Carbon	Per Cent Carbon	Per Cent Carbon	Per Cent Carbon	Per Cent Carbon	Per Cent Carbon	Per Cent Carbon	Per Cent Carbon
3 mil cut								
1st	1.13	0.86	0.08	0.87	0.29	0.04	0.05	1.13
2nd	1.11	0.88	0.04	0.99	0.41	0.04	0.03	1.04
3rd	1.13	0.93	0.07	1.06	0.49	0.05	0.03	1.08
4th	1.10	0.95	0.11	1.08	0.53	0.09	0.02	1.07
5th	1.13	0.99	0.30	1.09	0.58	0.14	0.04	1.08
10 mil cut								
1st	....	1.06	0.81	1.10	0.68	0.36	0.05	1.09
2nd	....	1.09	1.06	1.09	0.69	0.49	0.07	....
3rd	....	1.10	1.09	1.10	0.90	0.68	0.43	....
4th	....	1.12	1.10	1.14	1.02	0.77	0.62	....
5th	....	1.10	1.11	1.08	1.09	0.83	0.75	....
6th	....	....	1.13	1.10	1.09	0.84	0.85	....
7th	....	....	1.13	1.08	1.08	0.84	0.95	....
8th	....	....	1.09	1.06	1.10	0.86	1.04	....
9th	....	....	1.08	1.09	1.11	0.88	1.07	....
10th	....	....	1.02	1.09	1.10	0.97	1.10	....

weighed about 660 grams. Details of the treating furnace are readily seen in Fig. 1. Both ends of the silica tube are water-cooled and carry glass end pieces which are sealed on by use of high temperature wax. The heating zone is 24 inches long. This fact along with compensation for end effects in the furnace winding ensured uniform temperature over the entire length of the specimen.

The sample was placed in the center of the furnace and was supported 3/8 inch from the bottom of the silica tube by being bound to an alundum boat with nickel wire. This permitted free circulation of the gas around the sample. An insulated thermocouple placed alongside the sample inside the tube served to check the temperature, which was controlled by a couple outside the silica tube. The annealing chamber was thoroughly flushed out, the power was turned on and the gas flow maintained at 2 cubic feet per hour.

The temperature of anneal was 750 or 800 degrees Cent. (1380-1470 degrees Fahr.) and the duration of treatment 55 hours. A

Table VI

Analytical Data Taken From the Chromium Steel Samples (S.A.E. 52100) After Treating As Indicated

Sample	C1	C2	C3	C4	C5	C6	C10
Annealing Treatment	55 hrs. at 800° C	55 hrs. at 750° C	55 hrs. at 800° C	55 hrs. at 800° C	55 hrs. at 800° C	55 hrs. at 800° C	55 hrs. at 800° C
Annealing Atmosphere	Pure dry hydrogen	H_2 sat. with water	H_2 + 10 mg. water /cu.ft.	H_2 + 50 mg. water /cu.ft.	H_2 + 150 mg. water /cu.ft.	Pure dry hydrogen	H_2 saturated with water
Surface Ap. after anneal	Bright mirror-like	Blue grey	Dull dark green	Grey green	Grey green	Bright nirror-like	Grey
Location of sample	Per Cent Carbon	Per Cent Carbon	Per Cent Carbon	Per Cent Carbon	Per Cent Carbon	Per Cent Carbon	Per Cent Carbon
3 mil cut							
1st	0.96	0.24	1.03	0.57	0.12	0.92	0.06
2nd	0.98	0.53	1.07	0.63	0.30	0.95	0.05
3rd	1.01	0.59	1.09	0.69	0.36	0.94	0.06
4th	1.01	0.66	1.05	0.72	0.42	0.99	0.10
5th	1.04	0.82	1.06	0.79	0.46	0.99	0.10
10 mil cut							
1st	1.04	0.86	1.06	0.88	0.57	1.03	0.21
2nd	1.05	0.99	1.05	0.96	0.72	1.04	0.42
3rd	1.09	1.03	1.07	1.02	0.85	1.06	0.61
4th	1.06	1.06	1.04	1.04	0.87	1.08	0.82
5th	1.07	1.06	1.05	1.05	0.94	1.06	0.93
6th	....	1.06	1.06	1.07	0.92	1.07	1.02
7th	....	1.06	1.08	1.08	0.98	1.06	1.03
8th	....	1.08	1.09	1.10	0.97	1.07	1.03
9th	....	1.05	1.09	1.06	0.90	1.08	1.05
10th	....	1.05	1.08	1.06	0.99	1.08	1.06

back pressure of about 2 inches water was maintained in the treating furnace during each run. After the test, cooling was expedited by opening the furnace (split type).

All samples were studied by use of chemical analysis and metallographic tests. For the chemical analysis successive peripheral layers were removed and assayed for carbon. Each figure given is the mean of two or three results which checked closely. The complete analytical data with conditions of experimentation for the plain carbon steel are given in Table V and those for the chromium S.A.E. 52100 in Table VI.

The primary object of this analysis was to determine if pure dry hydrogen had any decarburizing effect on the surface of steel. It was considered also of importance to carry the investigation beyond the point studied by previous investigators, and hence to learn something about the influence of known amounts of water vapor on the decarburizing power.

In the general picture (Fig. 1) of the apparatus can be noted

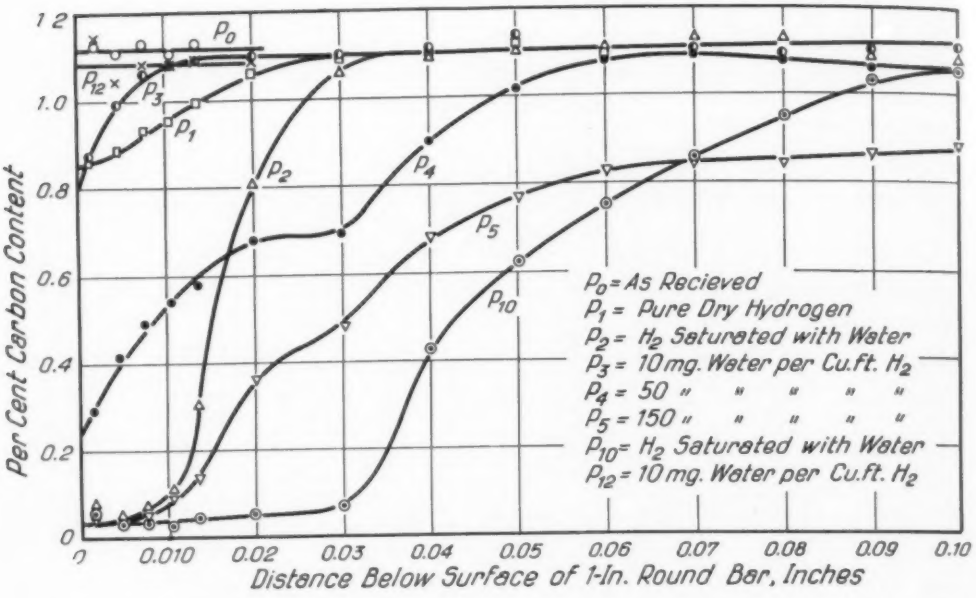
Per Cent Carbon Content
Distance Below Surface of 1-In. Round Bar, Inches
P_0 = As Recieved
P_1 = Pure Dry Hydrogen
P_2 = H_2 Saturated with Water
P_3 = 10 mg. Water per Cu.ft. H_2
P_4 = 50 " " " " "
P_5 = 150 " " " " "
P_{10} = H_2 Saturated with Water
P_{12} = 10 mg. Water per Cu.ft. H_2

Fig. 3—Graphical Illustration of Decarburization Data Presented in Table IV. P_2, P_3, Treated 55 Hours at 750 Degrees Cent. P_1, P_4, P_5, P_{10}, P_{12} Treated 55 Hours at 800 Degrees Cent.

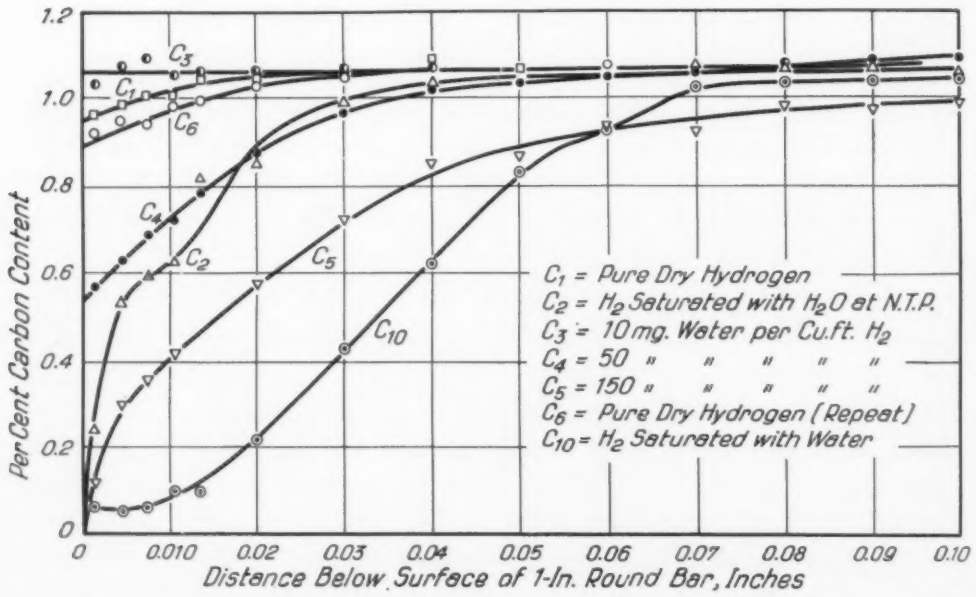
Per Cent Carbon Content
Distance Below Surface of 1-In. Round Bar, Inches
C_1 = Pure Dry Hydrogen
C_2 = H_2 Saturated with H_2O at N.T.P.
C_3 = 10 mg. Water per Cu.ft. H_2
C_4 = 50 " " " " "
C_5 = 150 " " " " "
C_6 = Pure Dry Hydrogen (Repeat)
C_{10} = H_2 Saturated with Water

Fig. 4—Graphical Illustration of Decarburization Data Presented in Table V. C_2 Treated 55 Hours at 750 Degrees Cent. C_1, C_3, C_4, C_5, C_6, C_{10} Treated 55 Hours at 800 Degrees Cent.

an electrolytic cell, a controlling rheostat, and a milliameter. The details of this part of the system are clearly shown in Fig. 2.

When completely dried gas is required needle valves c and e

remain closed and the purified gas passes via valve d to the treating furnace 14. Apparatus 9 is an electrolytic cell containing caustic potash. The electrodes are connected through a rheostat and milliameter to a 110 D.C. line. The voltage drop through the cell is so small a fraction of this voltage that line fluctuations can be neglected. The electrolyte is kept cool by immersion in an oil bath which is water-cooled by the jacket 12. A side stem permits addition of electrolyte, but owing to the pressure in the system, this stem must be closed during experimentation. The rate of electrolysis is controlled by the rheostat and measured by equivalent calculation from the milliameter reading. The products of electrolysis are swept along by the pure hydrogen passing through valve c on to furnace 13 and over the heated copper turnings. This material catalyzes the recombination of the electrolytic constituents to water again, whereby we have a gas with a predetermined water vapor content flowing through valve e and on through the experimental furnace 14.

It might be thought that water by evaporation would be carried over by the hydrogen. A check on this point was made by weighing the cell before and after experimentation. The loss in weight was about 2 or 3 per cent greater than that calculated by equivalence from the milliameter readings. This, of course, is a negligible amount in the experiments herein discussed.

All but two of the tests were run with 2 cubic feet per hour of hydrogen passing through the system. In the "saturated with water vapor" experiments, P2 and C2, a higher flow rate (3 cubic feet per hour) was used, due to the condensation of water in the ends of the test furnace with the consequent tendency to choke the system. In P10 and C10 2 cubic feet per hour was found to suffice.

By plotting the mean carbon content per cent of each successive peripheral layer analyzed, against the mean distance of the layer from the surface of the test sample a diagrammatic picture of the amount of decarburization and the depth of penetration is obtained. Figs. 3 and 4 present the data in this manner for the carbon and chromium carbon steels respectively.

Metallography of the Annealed Samples

Sections were cut from all the samples in order that the amount of surface decarburization and the depth of penetration might be

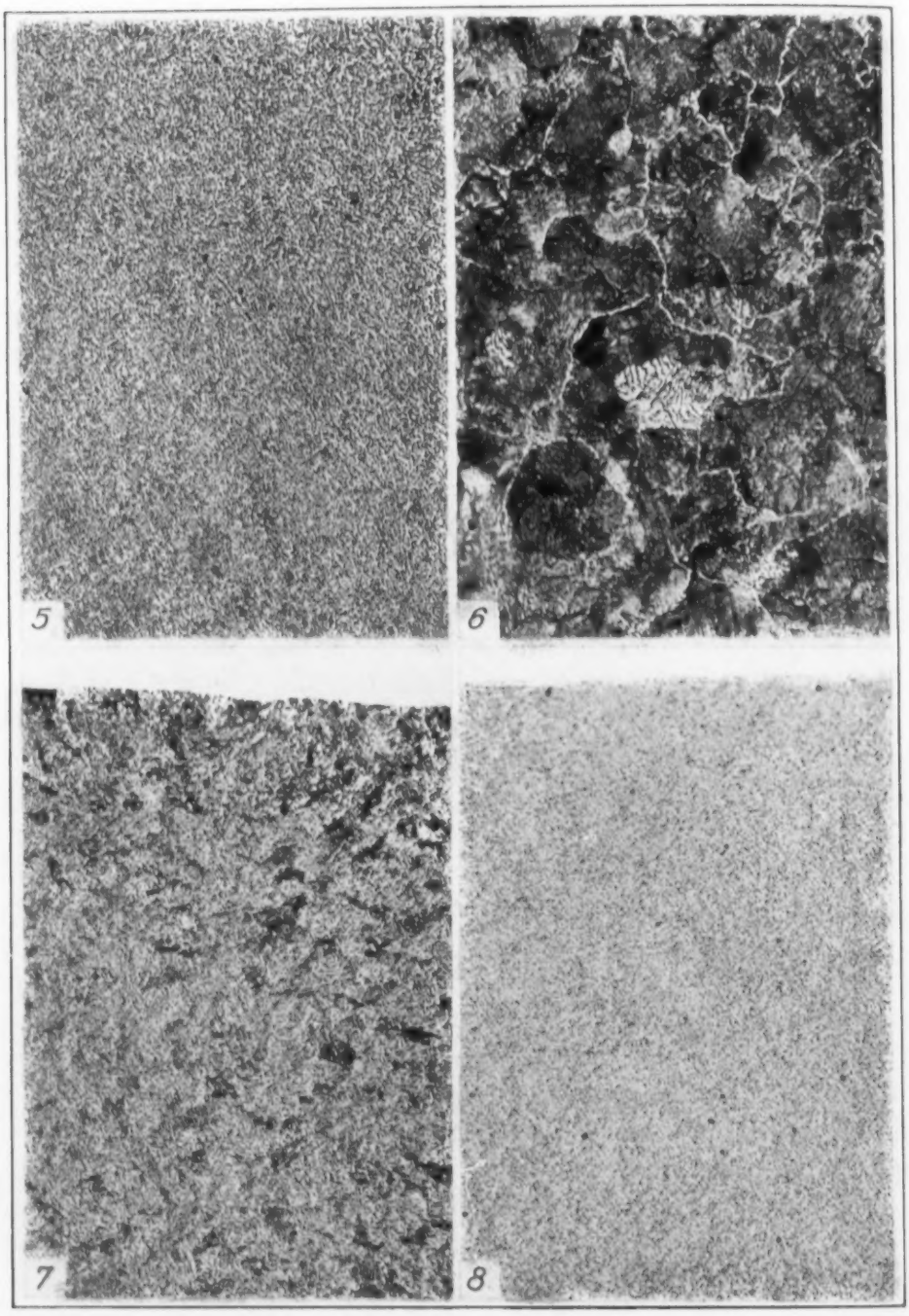

Fig. 5—Steel from the P2209. Plain Carbon Alloy as Received. Etched in Alcoholic Picric Acid. Completely Spheroidized. × 100.

Fig. 6—Section from the S.A.E. 52100. 1.4 Per Cent Chromium Alloy as Received. Etched in Picric Acid in Alcohol. A Slowly Cooled Structure. × 500.

Fig. 7—Sample P1. Annealed 55 Hours at 800 Degrees Cent. in Dry Hydrogen. Etched in Picric Acid. No Apparent Decarburization. × 100.

Fig. 8—Sample P3. Annealed 55 Hours at 750 Degrees Cent. in Hydrogen with 10 Milligrams of Water per Cubic Foot. Slight Decarburization Apparent. × 100.

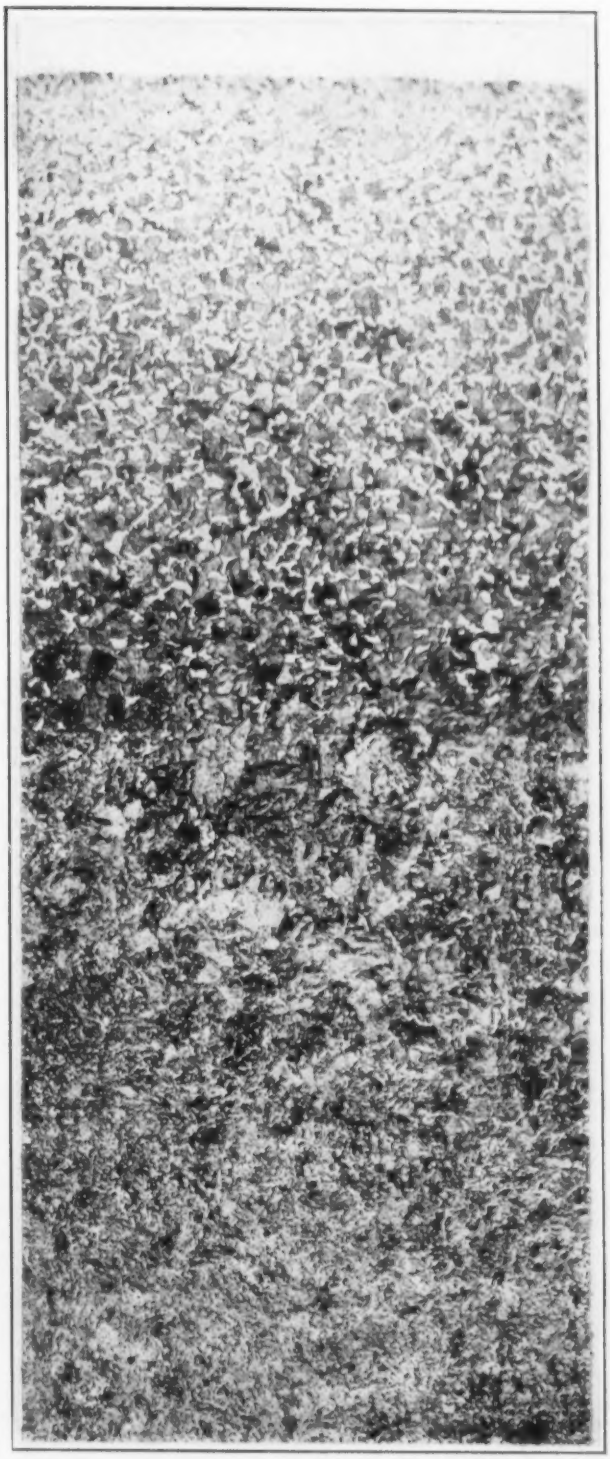

Fig. 9—Sample P4. Annealed 55 Hours at 800 Degrees Cent. in Hydrogen Containing 50 Milligrams of Water per Cubic Foot. Evident Signs of Marked Decarburization. Considerable Penetration. × 100.

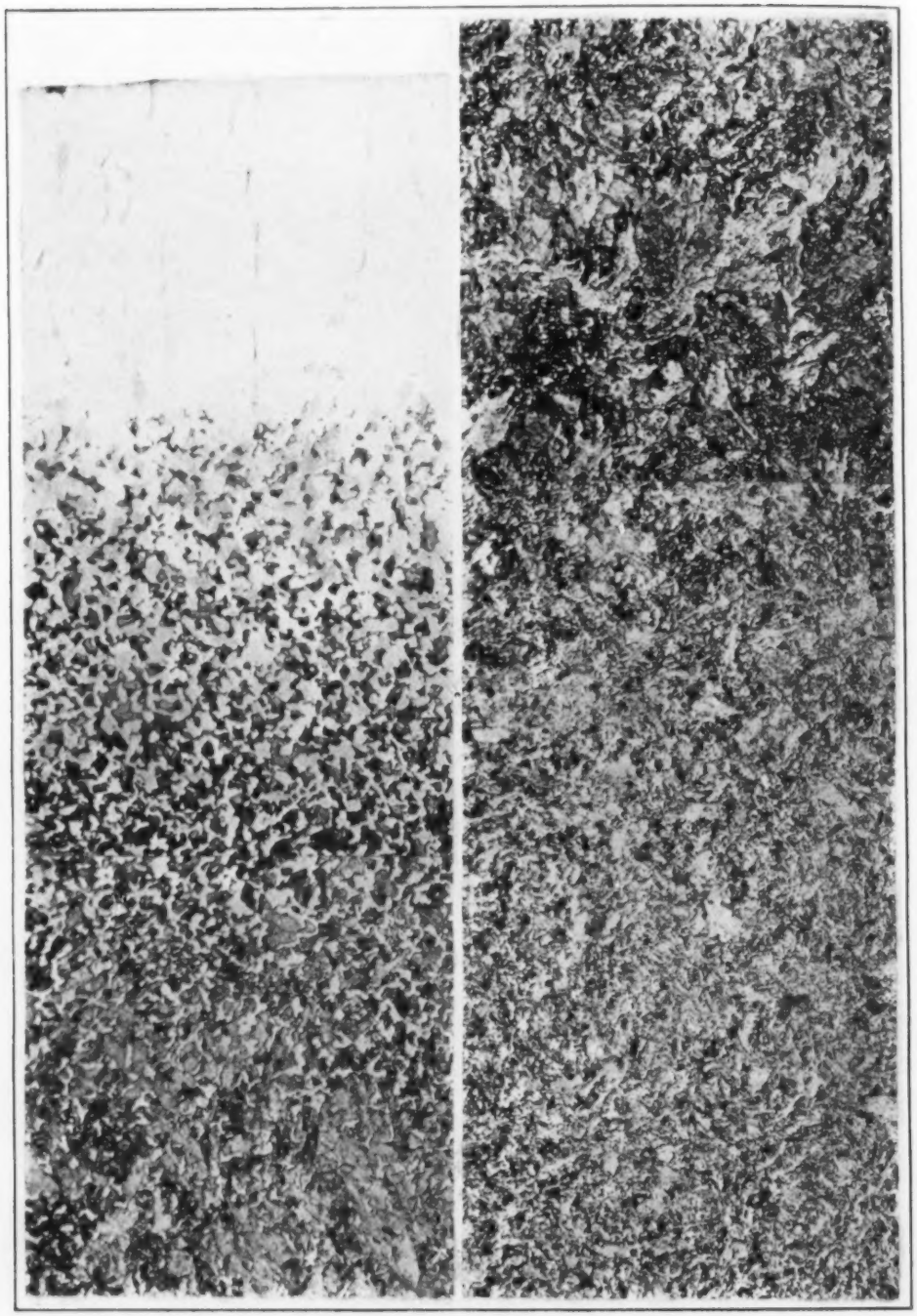

Fig. 10—Sample P5. Annealed 55 Hours at 800 Degrees Cent. in Hydrogen with 150 Milligrams of Water per Cubic Foot of Gas. Note Band of Free Ferrite and Extent of Decarburization. Top of Right Hand Strip Corresponds to Bottom of Left Hand Strip. × 100.

studied and correlated with the chemical analyses. The metallographic structures found in the rolled bars of the plain carbon and chromium steel are illustrated in Figs. 5 and 6 respectively. At 100 diameters the spheroidized structure of the carbon steel is evident. At 500 diameters it may be noted that the chromium sample is transformed into a fairly coarse pearlitic structure.

It has already been shown that by increasing the temperature

Fig. 11—Sample P2. Annealed 55 Hours at 750 Degrees Cent. in Hydrogen Saturated with Water Vapor. A Pure Ferrite Band with Limited Penetration. × 100.

of treatment an increase in decarburizing rate can be effected (see Experiments 13 and 17, Table I). It was considered that the maximum rate of increase would be observed on passing through the temperature range from below the eutectoid temperature to above the temperature where complete solid solubility was obtained. Accordingly 800 degrees Cent. (1470 degrees Fahr.) was selected for the

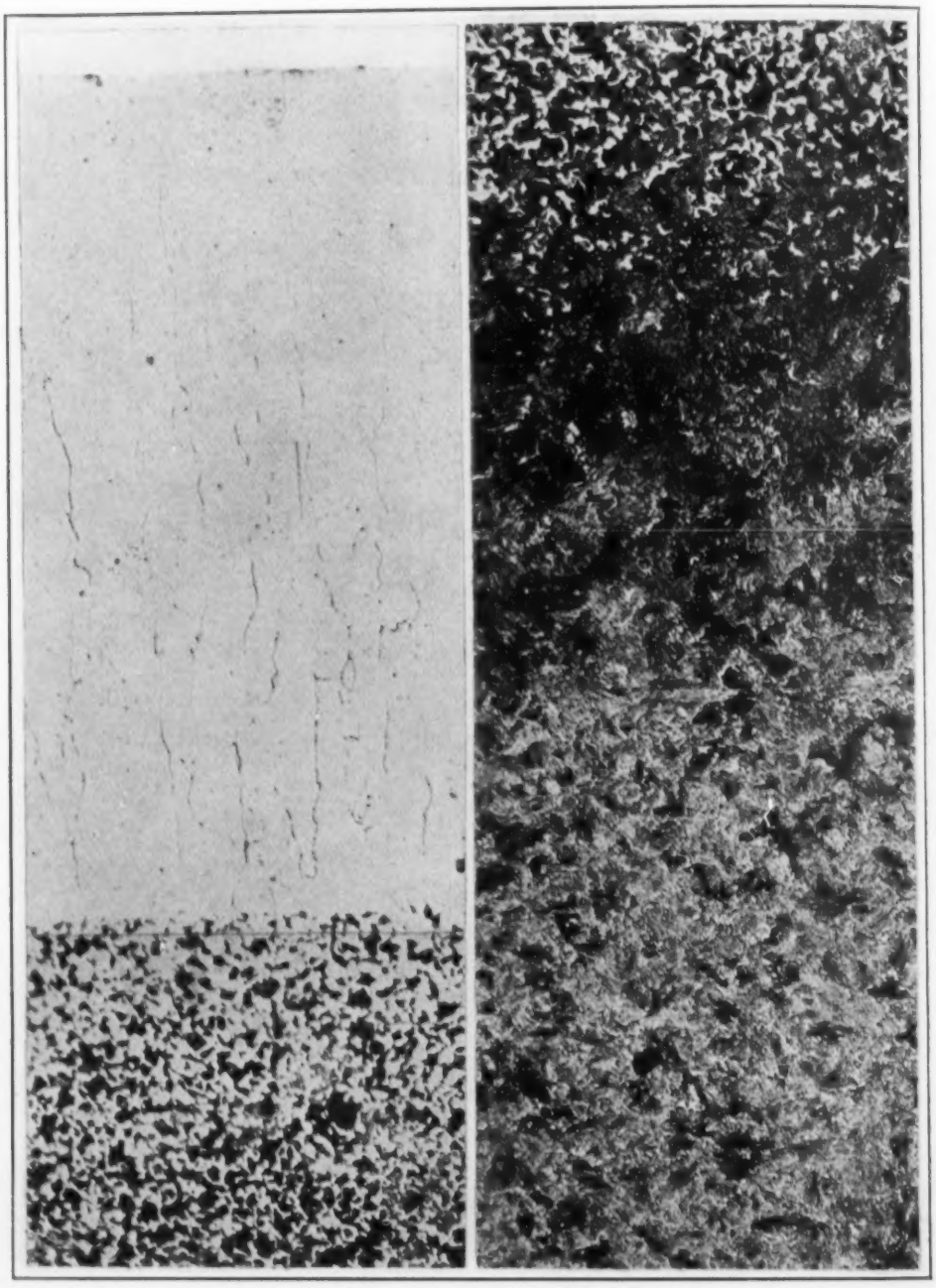

Fig. 12—Sample P10. Annealed 55 Hours at 800 Degrees Cent. in Hydrogen Saturated with Water Vapor. Note Band of Free Ferrite and Marked Penetration of Decarburization. Top of Right Hand Strip Corresponds to Bottom of Left Hand Strip. × 100.

major number of tests since dilatometric analysis of the steels showed that this temperature ensured a state of simple gamma solid solution (Fig. 22).

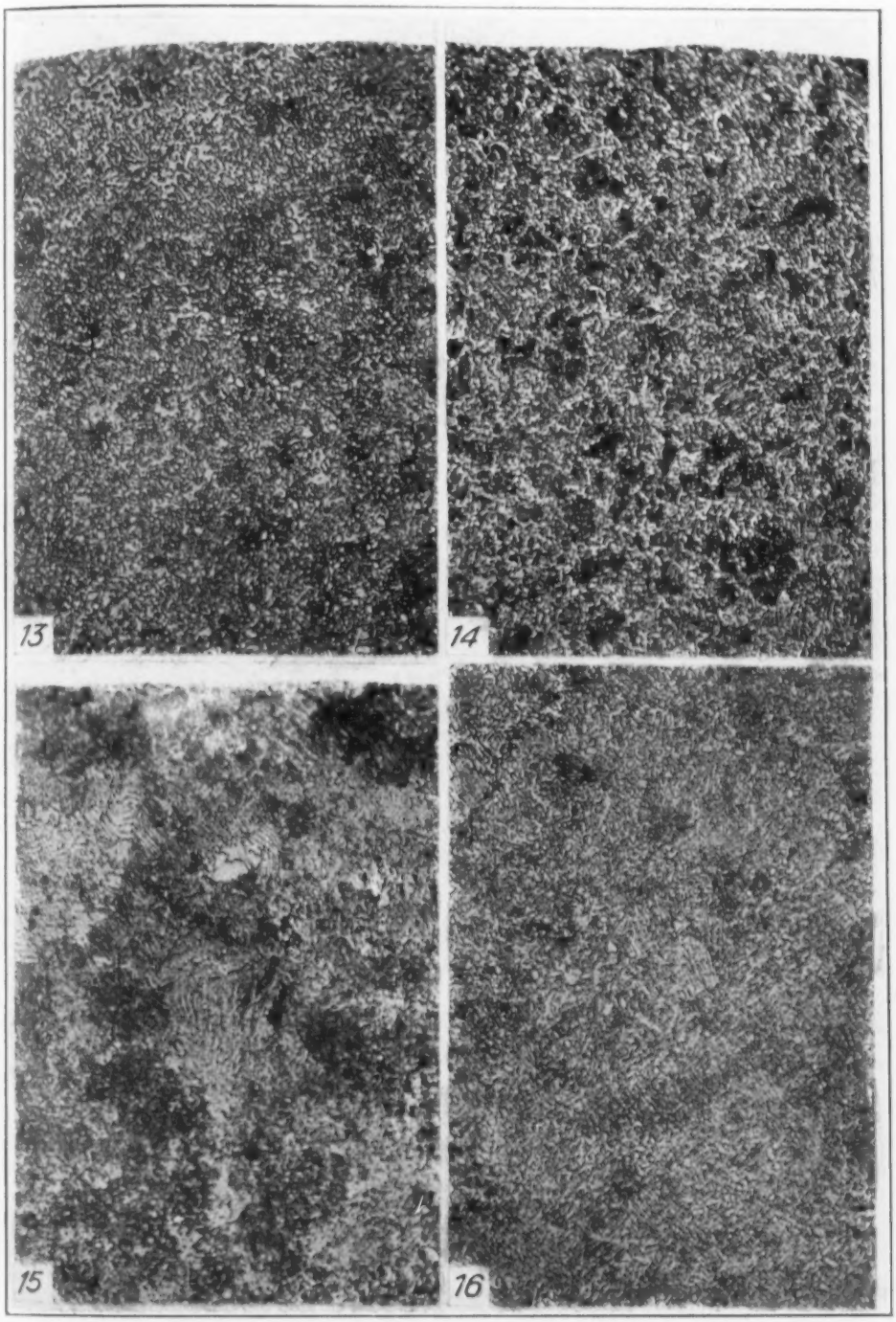

Fig. 13—Sample C1. Annealed 55 Hours at 800 Degrees Cent. in Dry Hydrogen. No Decarburization. × 500.

Fig. 14—Sample C3. Annealed 55 Hours at 800 Degrees Cent. in Hydrogen with 10 Milligrams of Water per Cubic Foot. No Decarburization. × 500.

Fig. 15—Sample C4. Annealed 55 Hours at 800 Degrees Cent. in Hydrogen with 50 Milligrams of Water per Cubic Foot. Limited Decarburization with Penetration. × 500.

Fig. 16—Sample C4. Structure of Interior of Sample Shown in Fig. 15. × 500.

Fig. 17—Sample C5. Annealed 55 Hours at 800 Degrees Cent. in Hydrogen with 150 Milligrams of Water per Cubic Foot. Marked Decarburization with Considerable Penetration. × 100.

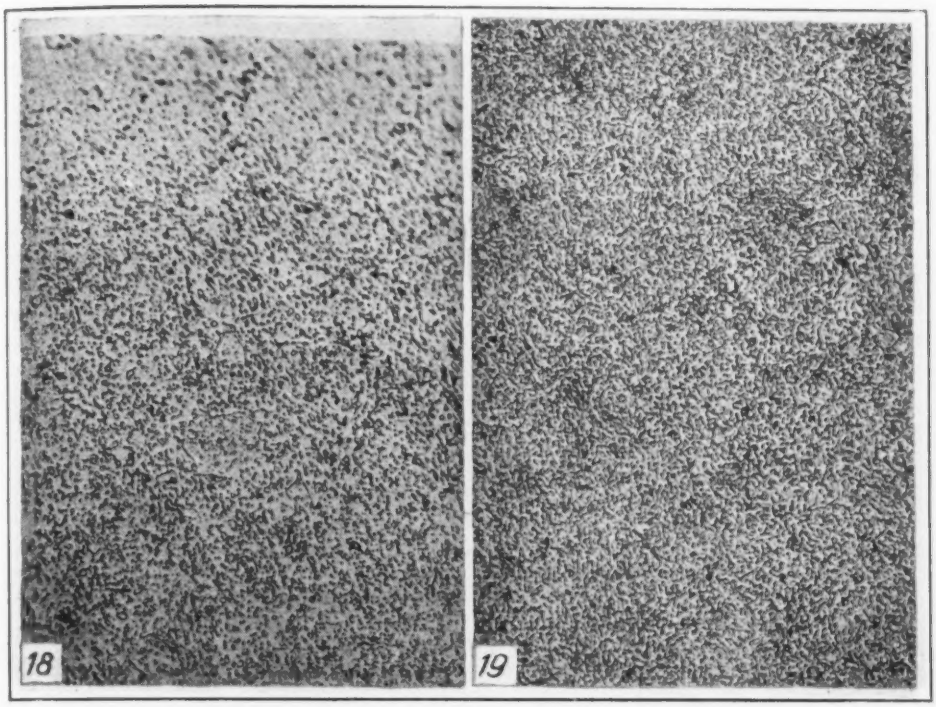

Fig. 18—Sample C2. Annealed 55 Hours at 750 Degrees Cent. in Hydrogen Saturated with Water. Definite Decarburization; Limited Penetration. × 500.
Fig. 19—Sample C2. Structure of Interior of Sample Shown in Fig. 18. A Spheroidized Structure. × 500.

The metallographic structures observed in the carbon series of decarburized specimens are shown in Figs. 7 to 12 inclusive. These structures should be correlated with the chemical data provided in Table IV and graphically depicted in Fig. 3. Figs. 7 and 8, showing the structures for pure dry hydrogen and hydrogen with 10 milligrams water per cubic foot, indicate practically no surface decarburization.

In Fig. 9 (50 milligrams water per cubic foot) there is no completely decarburized band of free ferrite, but partial decarburization extending into the interior of the steel is clearly evident. Fig. 10 (150 milligrams per cubic foot) shows a completely decarburized band of ferrite followed by the usual structure associated with decarburized steel. Fig. 11 cannot be so readily interpreted on account of the spheroidized structure from the 750 degrees Cent. (1380 degrees Fahr.) treatment, but the marked decarburization by hydrogen saturated with water vapor is obvious. Fig. 12 illustrates the metallographic structure of sample P10 which was also treated in hydrogen saturated with water vapor, but at a tempera-

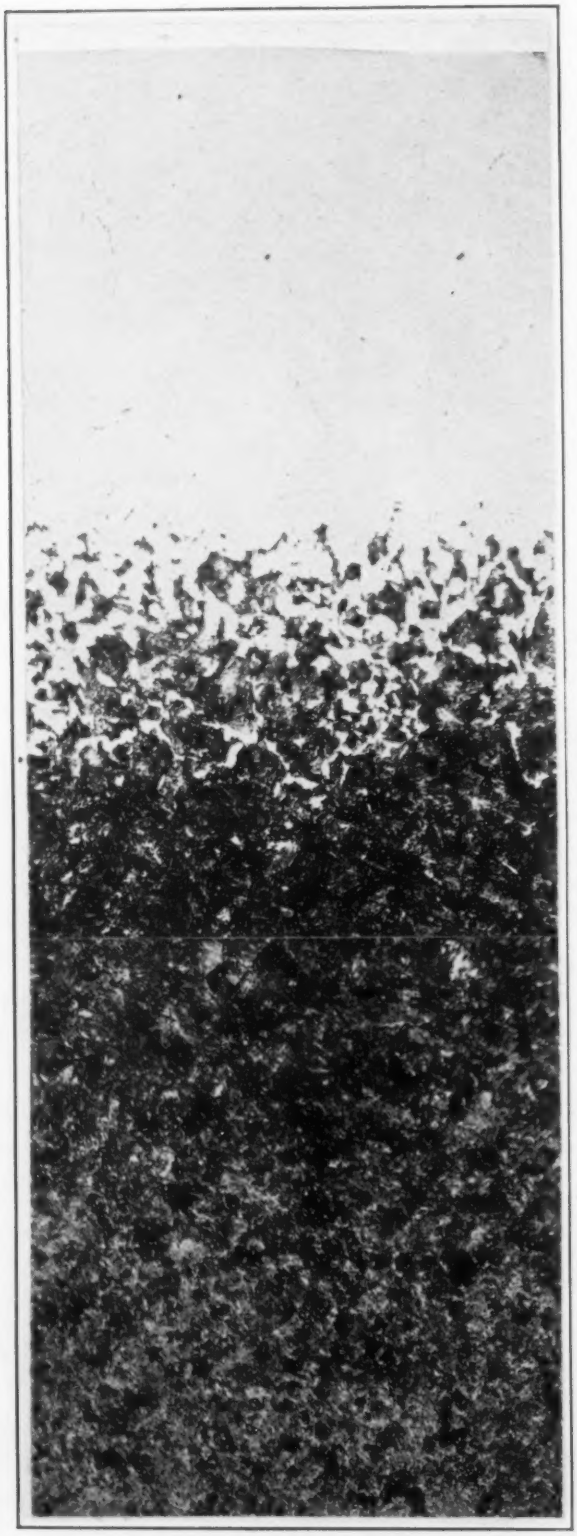

Fig. 20—Sample C10. Annealed 55 Hours at 800 Degrees Cent. in Hydrogen Saturated with Water. Marked Decarburization with Penetration. × 100.

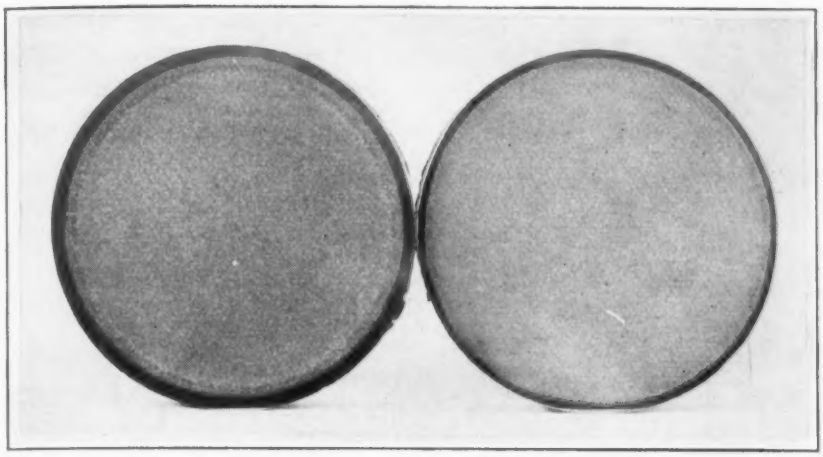

Fig. 21—Illustrating the Uniform Character of the Peripheral Decarburization Observed in Samples P10 (Left) and C10 (Right). × 1½.

ture of 800 degrees Cent. (1470 degrees Fahr.). It will be noted that in three of these samples composite photomicrographs at 100 diameters were required to illustrate the depth of penetration of decarburization.

The metallographic structures found in the chromium series of specimens are reproduced in Figs. 13 to 20 at 500 diameters with the exception of Figs. 17 and 20 (100 diameters).

Figs. 13 and 14 (dry hydrogen and hydrogen with 10 milligrams water per cubic foot) show no apparent decarburization (see Table V and Fig. 4). With specimen C4 (50 milligrams per cubic foot) there is a definite apparent but limited surface decarburization (Fig. 15). The structure in the interior of the sample is given in Fig. 16. With 150 milligrams water vapor the surface decarburization and the penetration are readily noted (Fig. 17). The spheroidized structure found in Figs. 18 and 19 (edge and interior) indicates marked surface decarburization and penetration from a treatment at 750 degrees Cent. (1380 degrees Fahr.) with hydrogen saturated with water vapor.

Fig. 20 illustrates a profound decarburizing effect of water vapor saturated hydrogen at 800 degrees Cent. on the chromium bearing steel. Fig. 21 indicates the uniform character of the peripheral decarburization obtained in samples P10 and C10.

Discussion of Results

During the course of the description of the tests some of the

experimental results have already been discussed. It is now proposed to draw attention to a few of the more salient features of the investigation.

The primary object of the research was to establish the role of water vapor in surface decarburization of steel by hydrogen. The preliminary experiments proved conclusively that ordinarily dry

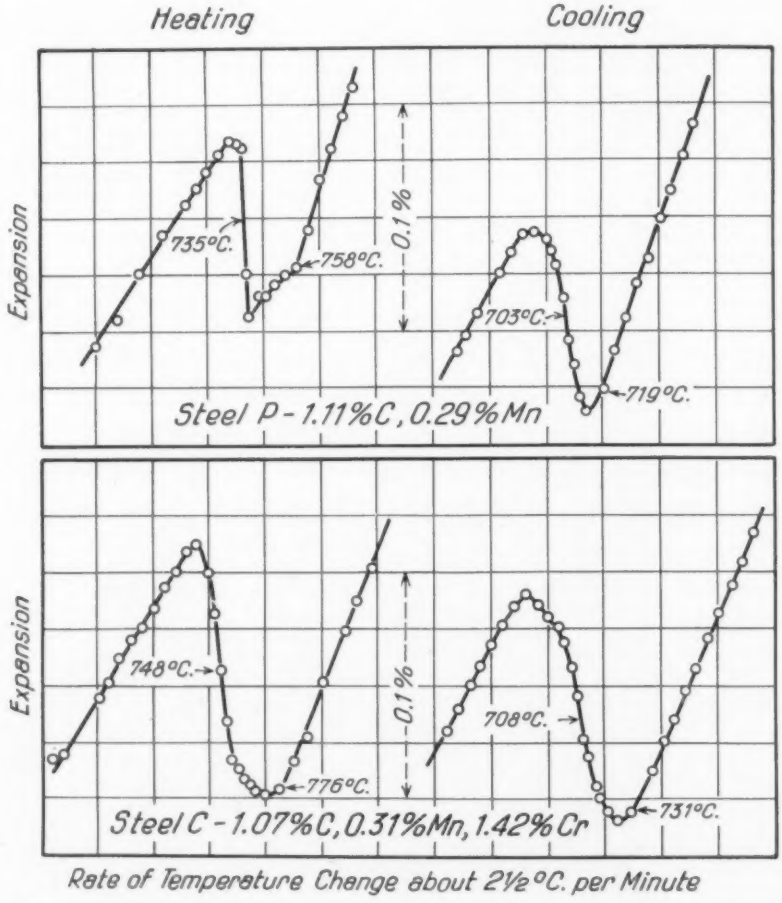

Fig. 22—Dilatometric Analyses of Steels Tested at 800 Degrees Cent.

hydrogen did not decarburize so effectively as moist hydrogen. Early experiments also demonstrated that ordinary dry hydrogen decarburized so slowly at 775 or 950 degrees Cent. (1425 or 1740 degrees Fahr.) even after several hours of test, chemical analysis was necessary to establish definitely that a reduction in peripheral carbon content had been effected.

Furthermore, the reduction was so limited as to lead to the suggestion that this slow rate of decarburization might be due to the

small amounts of impurities (oxygen and water vapor) which are difficult to remove. The staining tests, using heated strip iron and stainless steel, had previously received attention in the laboratories, and it was concluded that the presence of a few parts per million of free oxygen in hydrogen led to discoloration of bright cold-rolled mild steel strip in the course of a few minutes under suitable conditions of test.

It was also experimentally determined that stainless steel is susceptible to the familiar green tarnish in gas of such purity that iron is unaffected. The chromium alloy also reacts to traces of both oxygen and water vapor. It may therefore be concluded that hydrogen contains less than one part per million of these impurities when purified to that condition which fails to tarnish stainless steel when passed over a bright strip of the alloy, heated to a suitable temperature for a period of 60 minutes.

It is considered that this investigation constitutes a vigorous test of the decarburizing power of pure hydrogen so that a glance at the data demonstrates that hydrogen of the purity indicated has a real but limited decarburizing power, and that oxygen or water vapor materially serves to hasten the carbon eliminations. The basic chemical reactions are essentially as follows:

$$(1) \quad Fe_3C + 2\,H_2 = 3\,Fe + CH_4$$
$$(2) \quad Fe_3C + O = 3\,Fe + CO$$

the oxygen being derived from water vapor with the liberation of hydrogen. It may also be considered that this liberated hydrogen has stronger decarburizing characteristics than the hydrogen gas indicated in equation (1).

However it must be concluded that the reaction given in equation (1) must take place per se although at a very slow rate. Forquignon[11] has suggested that at a temperature of 1000 degrees Cent. (1830 degrees Fahr.) equilibrium between hydrogen, methane and free carbon corresponded with a mixture containing about 1 per cent methane and 99 per cent hydrogen. This limit was with carbon saturated steels. For non-saturated steels the proportion of methane would decrease. Thus with a steel containing 0.15 per cent carbon the percentage limit of methane in the mixture would be 0.1 per cent.

It is of considerable interest to investigate the relationship be-

[11]See discussion by H. LeChatelier on E. D. Campbell's paper, *Journal*, Iron and Steel Institute, 1919, No. 11, p. 415.

tween the weight of carbon removed from any one sample and the amount of oxygen passed through the system, in the form of water vapor, during the 55 hours' duration of experimentation.

Consider sample C4 where the hydrogen contained 50 milligrams water per cubic foot. Calculated total weight of carbon removed from the 660 grams (approximate) sample was under 0.25 gram. Total water passed through system was 5.5 grams which corresponds to 4.8 grams oxygen. The oxygen required to remove 0.25 gram carbon as carbon monoxide is ⅓ gram. Thus the amount of oxygen passed through the system was 15 times that theoretically required to oxidize all the carbon eliminated in the process of decarburization.

In sample C10 the maximum amount of carbon removed must be under 1 gram by weight. 1 gram carbon requires 1⅓ grams oxygen for combustion and this would correspond to 1½ grams water or a water content in the gas of about 14 milligrams per cubic foot. Many times this quantity was present in the gas.

It may also be shown that the carbon removal in sample P1 would require rather less than 1 milligram water per cubic foot to effect oxidation of all that carbon to carbon monoxide. However, it is certain that the water vapor content of the "pure dry hydrogen" used in this test could not contain water vapor to anything like that order of magnitude. This analysis thus further confirms the statement that pure hydrogen has a decarburizing power.

The results from samples P12, C1 and C6 are of special interest. On account of the very limited amount of decarburization indicated by chemical analysis in sample C1, treated in dry hydrogen, it was considered important to verify the result. Sample C6 provides data which confirm this definite but limited carbon elimination and indicate that pure hydrogen reacts with iron carbide, although hydrogen containing 10 milligrams water per cubic foot has apparently no decarburizing power.

In the case of the plain carbon steel the dry hydrogen (P1) has more effectively decarburized, but the 10 milligrams per cubic foot sample P12 again showed no decarburization. An apparent anomaly may be noted however in sample P3 decarburized at 750 degrees Cent. (1380 degrees Fahr.) in hydrogen with 10 milligrams water content.

The evidence strongly supports the contention that there is a small vapor content which has a minimum (or nil) decarburizing

power. Much more refined and exacting experimental data must be forthcoming before one may write dogmatically on this problem.

Another feature which should receive attention is the nature of distribution of the carbon from the periphery towards the center of the sample. This is well shown by the shape of the curves given in Figs. 3 and 4, and by the photomicrographs of the edges of the samples. The factors influencing this distribution appear to consist of both the element causing the carbon elimination and diffusion of the carbon itself towards the peripheral parts of the sample. The inflections in P2 and C2 (Figs. 3 and 4) which lead to a section of the curves assuming a position nearly parallel to the ordinate (rapid rate of increase in carbon content) are undoubtedly due to the slow rate of carbon diffusion at sub-critical temperatures.

Some years ago the writer[12] attempted to arrive at values denoting the diffusion constant or the specific rate of diffusion in iron with the following results:

At 650 degrees Cent.	D = 0.005
At 850 degrees Cent.	D = 0.05

From these data it may be inferred that the most opportune temperature for the formation of a pure ferrite peripheral band lies below the critical range since the carbon is but slowly replenished by diffusion. However the data show that the increase in the carbon-oxygen reaction far outbalances the increase in rate of carbon diffusion and results in the formation of the widest band of ferrite at the higher temperature.

In the P2209 series a ferrite band resulted when the steel was treated with moist hydrogen at 750 degrees Cent. (P2) and at 800 degrees Cent. (P10). In the S.A.E. 52100 a temperature of 800 degrees Cent. was necessary for the production of pure ferrite (C10). These are the only three tests which gave examples of this phenomenon.

It is well known that hydrogen diffuses into steel at temperatures of 400 degrees Cent. (750 degrees Fahr.) and upwards[13] but it is considered that the temperature of gamma solution range must be approximated before marked diffusion of oxygen takes place. It is possible that this low solubility or diffusion rate of oxygen in iron

[12] *Journal*, Iron and Steel Institute, 1922, No. 1, p. 131.

[13] Charpy and Bonncrot, *Comptes Rendus*, Vol. CLIV, 1912, p. 592-94, and *Comptes Rendus*, Vol. CLVI, 1913, p. 394-96.

at sub-critical temperatures is largely responsible for the slow rate of decarburization. It must be remembered of course that this gas penetration effect depends also on the facility with which the gaseous products of reaction can diffuse out of the metal again.

Of some commercial importance is the varying effect of moisture concentration on the surface appearance of the annealed samples. All specimens were subjected to test in the bright smooth machined condition. It is difficult to reproduce the surface appearance in photographic form; however, the surface description in Tables V and VI gives a fair idea of the conditions. It may be noted that the dry gas was the only condition which yielded a perfect mirror-bright anneal.

Acknowledgments

The author wishes to acknowledge his indebtedness to the Westinghouse Electric and Manufacturing Co. in whose research laboratories the work was conducted, for permission to publish the results. R. E. Shoup, an Intermediate Student, was responsible for much of the experimental work, Miss M. Ferguson prepared the photomicrographs, and R. H. Wynne conducted the chemical analyses. To P. H. Brace, the author is indebted for helpful criticism of the work.

DISCUSSION

Written Discussion: By J. B. Austin, Research Laboratory, United States Steel Corporation, Kearny, N. J.

The data reported by Dr. Austin are very interesting because they can be used to obtain an independent check on the diffusivity constant of carbon in iron as given by Bramley and Allen.[1] These authors, using a method much like that used by Mr. Austin, investigated the carbon gradient in steels decarburized in hydrogen between 850 and 1100 degrees Cent. and from their results were able to calculate the diffusivity constant for every 50 degrees Cent. within this range. The method of computation is based on the following solution of the well-known law of diffusion:

$$\phi = \frac{H}{\sqrt{4\pi\kappa t}} e^{\frac{-x^2}{4\kappa t}}$$

where ϕ is the decrease in carbon concentration at a distance x from the surface, t is the time of decarburization, κ is the diffusivity constant, and H is a numerical constant, related to the amount of carbon removed, which can be evalu-

[1]Bramley and Allen, *Engineering*, Vol. 133, 1932, pages 92-94, 123-126, 229, 305-306.

ated by methods described by Bramley and Allen. This relation should hold equally well for the data in Table I of the paper and a direct comparison has been made with sample P10. This sample was selected as the most likely to give good results because it represents a wide range of concentrations, because it is free from the irregularities found in some of the others, and because at 800 degrees Cent. most of it would be in the austenitic form. Bramley and Allen have shown that the logarithm of κ varies linearly with the reciprocal of the absolute temperature so that their data are easily extrapolated to 800 degrees Cent. The value so obtained is $K_{800} = 1.5 \times 10^{-8}$. The constant H, calculated from the decrease in carbon content at the surface, is 0.193. Substituting these values in the equation, the carbon content of the various cuts in P10 was calculated with results shown in the attached table, where they are compared with the experimental determinations given by Dr. Austin in his Table I. The value for the 6th cut as printed appears to be in error and it has been changed to conform with the curve of Fig. 1. The agreement is most satisfactory for all but the first two cuts. In this connection it should be noted that the low carbon content of these cuts indicates that at 800 degrees Cent. they must have been mainly ferrite, in which carbon presumably has a different diffusivity constant from that in austenite; agreement in this case is, therefore, not to be expected.

The agreement between observed and calculated values is obviously a confirmation of the diffusivity constants given by Bramley and Allen; and it also adds support to the view that in carburization or decarburization the reaction between metal and gas takes place only at the surface of the metal and that carbon diffuses through the metal only as carbon. The conception that hydrogen or oxygen diffuses into the metal, reacts with carbide or carbon, and then diffuses out as CH_4 or CO appears to be unsupported by experimental evidence. The factor which determines the maximum rate of decarburization is, therefore, the rate of diffusion of carbon. If the chemical reaction which takes place on the surface removes carbon very much faster than diffusion can supply it decarburization will proceed at its maximum rate; if, on the other hand, the reaction at the surface removes carbon only slightly faster than it is supplied by diffusion, decarburization will proceed slowly. The increase in decarburizing rate obtained by adding water vapor to hydrogen is presumably a consequence of the fact that on an iron surface the reaction $Fe_3C + H_2O = 3Fe + H_2 + CO$ proceeds more rapidly than the reaction $Fe_3C + 2H_2 = 3Fe + CH_4$.

The dips in the curves for P4 and P5 are very interesting, especially since Bramley and Allen obtained curves showing the same effect. They have considered the problem at some length and have concluded that they correspond to disturbances in the carbon gradient which occur during cooling through the critical range, and are not indicative of the gradient at temperature.

In conclusion, it is perhaps worth while to compare the diffusivity constant for one of the chromium steels C10 with that of carbon steel P10. A calculation based on the same equation gives $K_{800} = 1.0 \times 10^{-8}$ for C10, which is somewhat lower than K_{800} for P10, and gives quantitative expression to the common observation that carbon diffuses more slowly in chromium steels than in plain carbon steels.

Table A
Comparison of Calculated and Observed Carbon Contents for Sample P10

Cut	Per Cent Carbon Calculated	Per Cent Carbon Observed
1	0.11	0.05
2	0.23	0.07
3	0.39	0.43
4	0.58	0.62
5	0.76	0.75
6	0.90	0.85
7	1.00	0.95
8	1.05	1.04
9	1.08	1.07
10	1.10	1.10

Written Discussion: By A. L. Marshall, research laboratory, General Electric Co., Schenectady, N. Y.

In this connection attention should be called to a series of papers by Bramley and Allen[2]. These authors have studied the decarburizing of steels of carbon content 0.85, 1.08, 1.30 and 2 per cent in dry hydrogen, hydrogen containing 15 and 81 milligrams of water vapor per liter and mixtures of carbon monoxide and dioxide over a wide temperature range. In a previous paper the carburizing of steel was also investigated. Their results give quantitative support to the thesis that the role of the gas atmosphere is to remove carbon from or supply carbon to the surface of steel. The movement of carbon within the steel is caused by diffusion and can be quantitatively calculated. The kinks present in the concentration-depth curves as determined experimentally are the result of a redistribution of the carbon taking place during the cooling of the specimen. When the steel begins to cool, the surface layer being lower in carbon content is the first to undergo the γ-β transformation. Iron carbide being only slightly soluble in ferrite tends to be thrown out of solution. If, however, the change takes place sufficiently slowly, the carbide will diffuse to that part of the metal which has not yet undergone transformation. This process gives rise to a rapid local increase in concentration of carbide. Thus, by a kind of expulsion, all but a very little of the carbide present before cooling in the outer zone is driven inwards.

Written Discussion: By J. V. Emmons, chief metallurgist, Cleveland Twist Drill Co., Cleveland.

Dr. Austin is to be congratulated on his careful and painstaking research which explains many of the discrepancies noted in the results reported by previous investigators.

The results of the writer obtained in 1913 and 1914 to which Dr. Austin refers were obtained with hydrogen which had been freed from oxygen by passing through red hot copper foil, from CO_2 by passing through potassium hydroxide solution and from water by passing through a phosphoric anhydride tower. The examination for evidences of decarburization was made only by means of the microscope. When it was observed that the outside surface of the specimen was still hypereutectoid after annealing in this purified hydrogen for six hours at 2130 degrees Fahr., it was concluded that hydrogen was not a

[2]See footnote 1.

factor in the commercial decarburization of tool steel. No investigation was made to determine if there had been a minor amount of decarburization which still left the specimen with more than the eutectoid requirement of carbon. If the writer interprets Dr. Austin's results correctly, it is believed that they are in substantial agreement with his own limited experimental findings.

The point which Dr. Austin makes that there is a critical content of water vapor in hydrogen which exerts a minimum decarburizing action is very interesting. It may lead to increased refinements in the atmospheric control of furnaces used for particular annealing operations.

Written Discussion: By Clair Upthegrove, professor of metallurgy, University of Michigan, Ann Arbor, Michigan.

Dr. Austin is to be congratulated on his excellent paper on the role of water vapor in the surface decarburization of steel by hydrogen. Undoubtedly a great deal of the variance in the results of studies made in this and related fields where "dry gases" have been used is due to the latitude used in the interpretation of this term. This has been due partly to a lack of an exact knowledge of the drying powers of the agents used and partly to the lack of a ready and definite means of verifying the extent of the purification.

The use of stainless steel as the means of verification of the completeness of the removal of the water vapor and oxygen is novel, and at the same time emphasizes the important part very small percentages of these gases may play in the related phenomenon, scaling of steel.

The view advanced by Dr. Austin that there is a small water vapor content which has a minimum or nil decarburizing power is extremely interesting. Observations made in the carrying out of experimental work on scaling at the University of Michigan seemed to point to the possibility of there being a small water vapor content for certain scaling mediums which would give a minimum effect. As with decarburization a decrease in the moisture content normally results in a decrease in the amount of scaling. However as the amount of water vapor was reduced to very small percentages, a content appeared to be reached beyond which further very slight reductions brought about a correspondingly small increase in scaling. These observations were made when the water vapor content of the oxidizing agent was approximately of the same order as that at which Dr. Austin reports the minimum decarburizing effect, that is 10 milligrams per cubic foot or slightly less than 0.05 per cent by volume. The experimental procedure for determining these small differences in water vapor content however was not considered sufficiently refined to justify any conclusions.

CHAIRMAN R. G. GUTHRIE:[3] It is interesting to know that it is possible to bright anneal steel without decarburization under any circumstances. A few years ago we did not think that was possible. I see now that some work has been done that gives us hope again.

PROF. W. P. WOOD:[4] I have not read the paper thoroughly enough to be able to discuss it. There is one thing that came into my mind that I think probably you could answer, and that is in connection with retort carburizing.

As I recall, in a great deal of work in connection with gas carburizing and

[3]Metallurgist, Peoples Gas Light and Coke Co., Chicago.

[4]Professor of metallurgy, University of Michigan.

retort carburizing, you get better results in carburizing if you add a small amount of water at the beginning of the operation. Is that correct?

CHAIRMAN GUTHRIE: Yes, providing it was a very small amount. If you go over that amount, it begins to work the other way. Our work of a number of years ago was relatively crude compared to this of Dr. Austin but nevertheless there was quite a close agreement of that fact—that there is a critical amount of moisture that can be used. Not only that, but the main thing was to maintain the moisture constant because in gases the moisture does not stay the same from one time to the next.

PROF. W. P. WOOD: That is an interesting point. With a certain amount of water you get decarburization, and when you add more water you assist the carburizing process.

W. E. JOMINY:[5] The question just asked about whether you could get bright annealing and not decarburization with hydrogen prompted me to think of nitrogen. In some work we did about three years ago (which was published about two years ago) I studied decarburization with both nitrogen and hydrogen, in connection with a research carried out for the American Gas Association. I found that with pure dry nitrogen you obtain freedom from both scaling and decarburization. This nitrogen was dried by passing it through a U-tube of ascerite and three tubes of dehydrite (magnesium perchlorate).

As we were thinking of the usual heat treating cycles we used shorter periods of exposure than did Dr. Austin. In one hour's time and at a temperature of 1600 degrees Fahr. with pure dry hydrogen, we got no indication of decarburization. The hydrogen was dried by passing through ascerite and then magnesium perchlorate. A shiny mirror-like finish on the surface of the specimen was obtained. At 1800 degrees Fahr., however, after a 3-hour exposure in pure dry hydrogen we did get definite decarburization. This, I believe, will answer the question that came up a moment ago.

With moist hydrogen we, of course, got plenty of decarburization and the same was true with moist nitrogen. With nitrogen we happened to have used just about the same water vapor concentration as that used by Dr. Austin with hydrogen when he obtained his point of minimum decarburization. Our nitrogen had a concentration of 9 milligrams of water vapor per cubic foot of nitrogen. This mixture produced very definite decarburization at 1600 degrees Fahr. in one hour's time, the metallographic structure showing a layer of ferrite at the surface. It appears that water vapor is even more active in connection with nitrogen than with hydrogen.

This active decarburizing effect of water vapor is perhaps due to the presence of atomic hydrogen or atomic oxygen.

Another thing that is quite interesting is that if you prevent the formation of scale in a gas which will decarburize, you get a more active decarburizing effect. This might be an explanation of Dr. Austin's point of minimum decarburization with a very small quantity of water vapor since he reports the formation of a little colorization (oxidation) of his sample. When he prevents this small oxidation by completely eliminating water vapor, he obtains greater decarburization.

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[5]Metallurgist, A. O. Smith Corp., Milwaukee.

Perhaps the oxidation keeps up with the decarburization or possibly the oxide acts as a screen to slow up diffusion of the decarburizing gases. In the case of the atmosphere in a fuel fired furnace, if the atmosphere is adjusted to the point where you get almost no scaling you will find you have strong decarburization, much stronger than when scaling is produced.

Dr. Austin should be complimented on the painstaking and careful manner in which he pursued this research.

O. W. Ellis:[6] Mr. Jominy's observations regarding the effect of moist nitrogen on steel, I can fully confirm. In the experiments (the results of which I will describe tomorrow) at first we attempted to use an atmosphere of nitrogen without making any attempt to remove moisture from the nitrogen, and decarburization was most obvious.

Recently, in carrying out experiments, heating iron and steel wires in chlorine, we have found that the chlorine did not appear to affect the iron at all, but such moisture as was present in the gas reacted with the iron to form iron oxide, which was deposited on the walls of the vessel. In other words, though we had an amount of chlorine in excess of moisture, the substance that reacted with the iron at about 1000 degrees Cent. was the moisture and not chlorine.

I have one question to ask Dr. Austin. It appears that there is a limit to the decarburization of the alloys that he uses, which were hypereutectoid. This may be accidental. On the other hand, it may be due to equilibrium conditions.

Does he think that had he used hypoeutectoid steels the carbon content would not have fallen below the eutectoid content or below the solubility limit of carbon in gamma iron? I am suggesting that possibly it is the excess of carbon over the eutectoid content—that which was insoluble in gamma iron at 775 degrees Cent.—that may have given to dry hydrogen its decarburizing effect. Whether the slight trace of moisture in the hydrogen may have produced another equilibrium condition which resulted in no removal of carbon from the surface is also open to discussion.

You may gather from what I remarked just now that we have been trying to do work using nitrogen. In this connection we repeatedly requested that the nitrogen should be delivered to us as free from oxygen as possible. The cylinders were being delivered to us with the statement that they contained less than 0.1 per cent oxygen, and still we were having trouble with the nitrogen, although we thought that we had reasonably pure material.

We of course set out to discover what the oxygen content of the nitrogen was, and we found from 0.5 to 3 per cent. It appears that the suppliers were analyzing the nitrogen prior to its introduction into the cylinders, but they did not take any account of the possibility of oxygen being present in the cylinders at the time that they introduced the nitrogen. That, I think, is a trouble that will frequently be met with by those purchasing nitrogen and other gases from manufacturers of these gases. It is left to the user to determine what is the oxygen content of the material that he is using.

A. B. Kinzel:[7] Dr. Austin is certainly to be commended on his very precise study which has a very definite bearing on the bright annealing prob-

[6]Director, Ontario Research Foundation, Toronto, Canada.

[7]Metallurgist, Union Carbide and Carbon Research Laboratories, Long Island City.

lem. This problem, however, is much more complex than the discussion has indicated. One of the factors requiring careful consideration is the hydrogen concentration involved in the bright annealing gas.

Some of our work has shown that the lower the hydrogen concentration, the greater the amount of water vapor which may be present for a given degree of decarburizing power. However, if oxidation is taken into consideration, the components do not function in the same way; that is, to avoid tarnishing the surface, the higher the hydrogen concentration, the greater the amount of water vapor which may be present.

For most bright annealing work there is no reason for employing high hydrogen concentration. Mixtures of hydrogen and nitrogen present many advantages, one of which is the tendency to eliminate etch effects. The same is true with respect to decarburization. The avoidance of decarburization becomes simpler with lower hydrogen concentrations.

I should like to suggest that the quantitative data of the type which Dr. Austin has herewith submitted should be obtained on bright annealing mixtures in which the hydrogen concentration is appreciably lower.

H. A. SCHWARTZ:[8] Quite a long time ago we were interested in studying the reaction between hydrogen and oxygen in solid white cast iron. Nothing much came of the general study, but a portion of the procedure consisted of heating rather finely divided (perhaps 20 mesh) cast iron in a stream of hydrogen, and passing the outlet gases over iodine pentoxide, and collecting the carbon dioxide that was formed. We obtained what we thought we were going to have in the first place, which was that this was an oxidation of carbon monoxide which came from oxygen and carbon in the iron, but also the reaction $2H_2 + Fe_3C = 3Fe + CH_4$ will go on indefinitely. We finally used tank hydrogen, which was dried over sulphuric acid, and by passing through liquid sodium-potassium alloys. The methane came off as merrily as ever, and would go on coming off as long as experiment was continued, and would come off even if you dropped the temperature to a few hundred degrees Cent., so that in cases where you had free cementite as a phase, evidently with whatever degree of purity of hydrogen we secured by the particular procedure, continued to take out carbon just as long as you wanted to continue the experiment.

A. W. SCHLUCHTER:[9] I should like to ask Dr. Austin if he has any data on the oxygen content of commercial hydrogen, including both free oxygen and also that combined as water vapor. I should also like to ask him if he has any data on the water content of the gas made by cracking commercially dry ammonia.

Author's Closure

I am pleased to have the discussions by J. B. Austin and A. L. Marshall. Both these gentlemen touch on the same problem, but in a different manner. The former gives us a glimpse of the mathematical analysis of Bramley and Allen, while the latter provides us with a simple though lucid explanation from

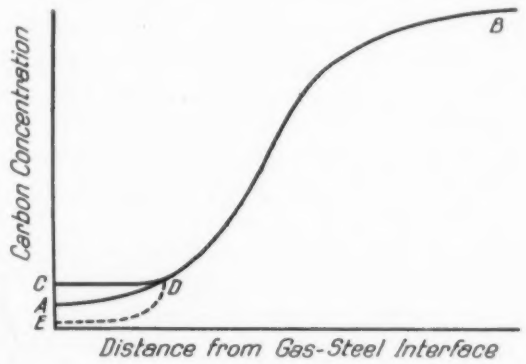
[8]Manager of Research, National Malleable and Steel Castings Co., Cleveland.

[9]General Motors Research Laboratories, Detroit.

those authors' paper to account for the kinks or changes in direction noticed in the concentration-depth curves.

I have been aware of this cited paper, but as the work did not appear in print until about the completion of the work reported in my paper, I did not unfortunately have the advantage of Bramley and Allen's data in planning our own investigation. The comparison between the observed and calculated carbon contents for the sample P10 is extremely interesting. Very good agreement is obtained over 8 of the 10 values cited by Mr. Austin, but it is in the first two peripheral cuts where the divergence occurs. During the week I examined the data of Bramley and Allen and found a similar discrepancy between observed and calculated carbon content of the first one or two cuts.

I thank Mr. Austin for drawing attention to the error in one value given under P10. This has been corrected. However, Mr. Austin is misinterpreting the data when he considers the 1st 10 mil cut to be the first peripheral cut taken



on the sample. This first 10 mil cut was taken after the five .3 mil cuts. In this case the discrepancy between calculated and observed values for carbon concentration at different peripheral layers is still more marked. Mr. Austin appears to wish to disregard these observed low carbon concentrations at the surface and assume that the data show proof that the chemical reaction causing decarburization occurs only at the gas-metal interface and that carbon is eliminated from the interior only by diffusion toward the periphery.

Mr. Marshall suggests that the kinks in the curve are the result of carbon distribution due to carbon moving inwards from the peripheral carbon-denuded ferrite areas (at 800 degrees Cent.) to the interior austenitic regions where high solubility for carbon is found. He uses this idea to account for the peripheral band of nearly pure ferrite.

My own view of the formation of this ferrite, therefore, appears to be opposed to those of the discussors and I believe a consideration of the diffusion curve supports my contention that decarburization is partly accounted for by the supposition that the carbon reaction takes place within the steel as well as at the gas-iron interface.

The general type of diffusion curve is shown as A B.

The curve obtained from experimental data exhibits a definite deviation as B C. The point D may be assumed to be the location where we have the presence of ferrite CD and austenite DB in juxtaposition.

If the problem is one purely of diffusion should we now have a high C concentration at D, and moving in the direction D A at first a steep concentration gradient as DE due to the slow diffusion rate of carbon in ferritic iron? Experimental evidence strongly indicates the presence of a very limited concentration gradient and that this limited gradient can be accounted for only by the assumption that we have gaseous penetration within the steel and removal of carbon by diffusion of the products of reaction.

A reference to Fig. 3 in the paper is of interest in this connection.

I should like to have given experimental consideration to the effect of temperature on the phenomenon discussed but a research of this kind involves a large amount of careful experimental work. Each of the chemical analyses for carbon recorded represents the mean of three determinations. Perhaps I should mention that 800 degrees Cent. was selected because it is about the temperature used to obtain spheroidization in commercial high carbon steels.

Professor Wood raises the question of carburization. There is nothing in the present paper on this phase of the work but we have had some very interesting results on carburizing plate. It seems that to get a "tight coat" in galvanizing it is necessary to put back a little carbon into the surface of the sheet. Our experiments with certain hydrocarbons mixed with hydrogen lead us to find that we could get, under the right conditions (and those conditions include little water vapor) complete carburization right through the sheet of about 18 gage in 30 minutes, with the sheets coming from the furnace in a bright annealed condition. Thus, we were obtaining bright annealing and heavy carburization at the same time.

I thank Professor Upthegrove for his kind remarks. The reference to a critical water vapor content of an atmosphere which leads to minimum scaling at elevated temperatures appears to be very significant. Determinations of minute amounts of water vapor are difficult and it is felt that stainless steel provides an ultra-sensitive qualitative test.

In his work some 20 years ago, Mr. Emmons concluded that dry hydrogen did not lead to pronounced decarburization during anneal. The present work undoubtedly confirms that conclusion. Mr. Emmons refers to the application of the data to the anneal of commercial steels.

With the few brief comments at the end of my presentation of the paper, I hope that I have demonstrated a real practical application for the results of our investigation.

The author thanks Mr. Jominy for his suggestion of the possible screening action of thin oxide films in decarburization. With respect to the decarburizing action of moist nitrogen it would seem that the water vapor is wholly responsible for carbon elimination. Furthermore, it must be borne in mind that the critical water vapor content may depend on the temperature at which the analysis of this phenomenon is conducted.

Many dehydrating agents purify satisfactorily for many purposes, but I do not think that I have found anything better than activated alumina. I believe the low vapor pressure of water after passing through activated alumina reduces the water to as low a value as by any means we have, other than the liquid air trap method.

Mr. Schluchter asks for data on water content of gases, and I suppose Mr. Kinzel could advise us on this matter. In the case of tank hydrogen it is a little difficult to state just what the water vapor content is. Sometimes we are able to pour water from the cylinders; at other times the gas appears to be "quite dry."

I suppose many of us accept the oxygen content of commercial nitrogen at about 0.5 per cent, and do not regard tank nitrogen in any sense as a pure gas.

With regard to the cracking of ammonia it is not possible to give the water vapor content, as this depends on the condition of the cracker. Iron is usually used as the catalyst, but it is charged into the dissociator chamber as iron oxide which is gradually reduced to free iron. In the early stages of the use of this dissociator the dissociated ammonia is saturated with water vapor. After the dissociator has been in use some time a fairly dry nitrogen-hydrogen mixture is obtained. In some of our experimental work we had gas from the dissociator showing a dew point of about minus 40 to 50 degrees Cent. In terms of water vapor this means something of the order of perhaps 5 milligrams per cubic foot.

It is difficult to state whether the decarburization in pure hydrogen, to a value on the peripheral parts of the steel approximately equal to that of eutectoid composition, as pointed out by Prof. Ellis, is fortuitous or not. His comments on moist chlorine are interesting.

Mr. Kinzel raises the question of low hydrogen concentration which has commercial importance in industrial bright anneal. However, the author cannot quite follow the suggestion that lower hydrogen concentrations permit greater water vapor concentrations for the same degree of decarburizing power, since the oxidizing power of hydrogen-water vapor mixtures depends on the ratio of these substances present in a gas. Thus for any given temperature if the water-hydrogen ratio is above a given value a steel is oxidized in that atmosphere. If bright anneal is desired the value must not be exceeded, so that when the hydrogen concentration is halved the water vapor concentration must also be halved. Otherwise oxidation of the steel occurs, and oxidation results in increased decarburization. The author has not encountered the hydrogen etch trouble in steel to which Mr. Kinzel refers.

The carbon-hydrogen reaction mentioned by Dr. Schwartz is to be expected, although at elevated temperatures one may be sure that the methane concentration will be very low.

Mr. Guthrie refers to carburization. The present paper of course deals exclusively with decarburization by hydrogen containing limited amounts of water vapor. The atmosphere resulting from the reactions between gas, and carbon in the metal produce atmospheres which are actually carburizing to steels of lower carbon content. The concomitant decarburization of steel and the carburization of iron wire surrounding the steel was discussed by the present writer in his cited paper before the British Iron and Steel Institute in 1922.

Finally, the author would like to acknowledge the kind reception of his paper and to sincerely thank the many members of the Society who contributed so freely to the discussion.

SOME PROBLEMS OF QUENCHING STEEL CYLINDERS

By Howard Scott

Abstract

There are seven factors of major importance which determine the cooling rate within steel cylinders during quenching. They are interrelated in a manner explicitly defined by the laws of heat conduction from which the general relations were calculated. These results are given in condensed tabular form from which the effect of each variable on the cooling rate can be readily deduced.

In order to apply these data to the solution of specific problems, the thermal constants of representative steels and of several important quenching media were evaluated approximately. The values obtained were used to show how the cooling rate at the center of a cylinder and at a crucial temperature varies with the quenching medium and diameter of cylinder. Effects of the same variables on cooling rate distribution were also expressed as a contribution to the problem of quenching shallow hardening carbon steels. Several other questions regarding the hardening of steel are amenable to study in the same manner.

I. Introduction

THERE have arisen in connection with the quenching of steel a number of problems which require for their solution a knowledge of the cooling rate distribution within simple shapes during quenching. Several of general interest may be mentioned. Does an increase in quenching temperature actually produce faster cooling as is apparently implied by the resultant deeper hardening? What is the ultimate limit of cooling rates attainable in steels by increasing the quenching power of quenching media? What is the sequence of transformations in shallow hardening steels?

The foregoing and related questions can be answered by a study of cooling rate distribution during the quenching of a simple shape as affected by the important variables of quenching: size of piece, kind of quenching medium and quenching temperature. These and

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related problems are considered here: the others in a subsequent paper.

Two methods for obtaining the required data may be considered. First, one might determine experimentally the cooling rate at various positions within appropriate shapes as one after the other of the major variables are changed. This method, however, is too laborious for so extensive a project as is outlined here. Also the technique is very difficult and subject to considerable uncertainty. Fortunately another method is available which permits broad deductions from a minimum of experimental observations.

An alternative method is the calculation of cooling rates from the equations of transient heat flow developed on the assumption that the temperature gradient at the surface of the piece quenched is proportional to its surface temperature. This method too involves experimental work, namely, the evaluation of the essential thermal constants of the steel and the quenching media concerned. These determinations are quite practicable and apply for most sizes and shapes. The method is essentially one of interpolation and extrapolation from experimental observations of cooling rate.

Certain objections[1] have been raised to the application of mathematical analysis, namely: that the constants of both the steel and the bath change with temperature and that transformations involving an evolution of heat occur during quenching. Both objections are valid if one assumes that determination of cooling rates throughout the whole duration of the quench is necessary to solve vital problems. The first objection can be dismissed, however, if consideration is restricted to a limited temperature range. Heindlhofer[2] has already shown this. In the problems discussed here, one is concerned only with the cooling rate before any transformation starts which eliminates the second objection. Certain precautions must be observed in using the analytical method and are noted.

II. Variables of Quenching

The theory of heat conduction embraces the important variables of quenching as follows:

Ti = initial or quenching temperature
To = final or bath temperature
T = temperature at a given position and time after start or quench.

[1]Portevin and Garvin, *Journal*, Iron and Steel Institute, Vol. 99, 1919, p. 469.

[2]Heindlhofer, *Physical Review*, Vol. 20, 1922, p. 221.

It does not recognize any difference due to absolute temperature range except as the range affects the thermal constants. Consequently, one temperature variable can be substituted for the three already given by writing:

$$U = \frac{T - To}{Ti - To} = \text{temperature ratio}$$

Cooling rate at the temperature T is now given by

$$\frac{dT}{dt} = (Ti - To)\frac{du}{dt}$$

The other important variables may be expressed by the following symbols:

t = time at which temperature has fallen to T degrees in seconds after start of quench.

a^2 = diffusivity of the steel

$$= \frac{\text{thermal conductivity}}{\text{specific heat} \times \text{density}}$$

h = quenching constant of bath

The quenching constant is defined by the relation:

$$h = \frac{H}{K} = -\frac{1}{u} : \frac{du}{dr}$$

Since K is the thermal conductivity of the metal, the quenching constant of the bath is determined in part by it. The thermal conductivity of steels, however, does not vary much within normal composition limits, so in most cases h can be considered as a representative property of the bath only. Were a steel of abnormal thermal conductivity concerned, h may be appropriately modified by means of the relations given.

The variables fixing position within the body studied of course depend on the shape of the body. Here consideration has been restricted to the long cylinder because it is the shape most studied experimentally and because it is the simplest excepting only the sphere. Two additional variables suffice to express position and size for this shape, namely:

b = half diameter of cylinder
r = distance from axis of point at temperature T

The relations deduced apply only to points remote from the ends of cylinders whose lengths are at least several times their diameters. The equations expressing the relations between the foregoing variables are given in the appendix at the end of this paper. It may be noted that 9 variable factors are involved. The computations are rather laborious, but once made in a general form there is no further need for using the equations. These computations have been made and the simplified results are given in Tables I and II. Similar computations have been made[3] for cooling times but not for rates which are our chief concern here. The cooling times are given here for the sake of completeness and because they are calculated to a greater accuracy than previous data. The values tabulated can be plotted in a variety of ways to show the specific effects of the individual variables as is done for certain ones of immediate interest.

Simplification permitting the compact presentation of results in the tables is possible due to the fact that the temperature ratio U is a funcion of $\frac{a^2t}{b^2}$ only with a given value of hb and the cooling rate term, $\frac{b^2}{a^2} \cdot \frac{du}{dt}$, is a function of U only with a given value of hb. For the purpose of illustration a generalized set of time-temperature curves for hb = 10 is plotted in Fig. 1 and of cooling rate-temperature curves in Fig. 2. This value of hb is representative of a 1 inch diameter cylinder quenched in a strongly agitated water bath. Each curve represents a position within the cylinder identified by its distance from the center with respect to the cylinder radius. For the same quench and another size, a set of curves for another value of hb is required. Data have been calculated for a sufficient number of values of hb so that cooling times and rates may be found for intermediate values by interpolation.

In the later stages of a quench the cooling rate throughout the steel becomes proportional to the temperature, Newton's law of cooling, providing no transformation occurs and the thermal constants do not change with temperature. Cooling under this condition is very simply expressed as shown in the appendix. Cooling rates for this status are given in Fig. 3 and the temperature limits below which they may be applied in Fig. 4. After the quenching constants are

[3]Gurney and Lurie, *Journal*, Industrial and Engineering Chemistry, Vol. 15, 1923, p. 1170. Gröber, H., Y. Ver. Deut. Ing., Vol. 69, 1925, p. 705.

Table I

Calculated Relations Between Time, Temperature, Diameter of Cylinder, Position Therein and Cooling Constants for Long Cylinders so Cooled That Temperature Gradient at Surface is Proportional to Surface Temperature

	Values of $(a^2 t)/b^2$ for U =						
r/b	0.90	0.80	0.70	0.60	0.50	0.40	0.30
				hb = ∞			
0	0.087	0.114	0.140	0.168	0.201	0.239	0.290
0.5	0.039	0.057	0.079	0.103	0.133	0.170	0.220
0.7	0.016	0.024	0.035	0.047	0.066	0.096	0.139
0.8	0.008	0.012	0.017	0.024	0.035	0.051	0.081
0.9	0.003	0.004	0.005	0.007	0.010	0.015	0.027
1.0	0	0	0	0	0	0	0
				hb = 10			
0	0.100	0.133	0.166	0.201	0.241	0.287	0.348
0.5	0.051	0.076	0.102	0.134	0.173	0.220	0.279
0.7	0.023	0.037	0.053	0.075	0.105	0.145	0.204
0.8	0.014	0.021	0.032	0.046	0.067	0.098	0.146
0.9	0.006	0.009	0.013	0.021	0.031	0.049	0.083
1.0	0.001	0.002	0.003	0.004	0.006	0.011	0.022
				hb = 5			
0	0.111	0.151	0.188	0.228	0.275	0.332	0.405
0.5	0.059	0.092	0.125	0.162	0.210	0.265	0.340
0.7	0.029	0.048	0.072	0.103	0.142	0.194	0.263
0.8	0.017	0.029	0.045	0.067	0.099	0.145	0.212
0.9	0.007	0.013	0.023	0.035	0.057	0.091	0.147
1.0	0.002	0.003	0.005	0.010	0.021	0.039	0.074
				hb = 3			
0	0.123	0.170	0.216	0.266	0.327	0.395	0.485
0.5	0.072	0.112	0.154	0.201	0.259	0.331	0.417
0.7	0.037	0.063	0.096	0.139	0.192	0.258	0.349
0.8	0.022	0.040	0.066	0.101	0.146	0.210	0.298
0.9	0.010	0.021	0.036	0.061	0.099	0.154	0.236
1.0	0.003	0.006	0.013	0.026	0.051	0.092	0.161
				hb = 1.6			
0	0.149	0.210	0.275	0.347	0.428	0.528	0.657
0.7	0.052	0.095	0.148	0.212	0.294	0.395	0.525
0.9	0.016	0.040	0.075	0.130	0.201	0.300	0.427
1.0	0.005	0.015	0.040	0.080	0.143	0.232	0.358
				hb = 1.0			
0	0.176	0.259	0.345	0.441	0.560	0.700	.....
0.7	0.072	0.138	0.219	0.314	0.430	0.575	.....
0.9	0.027	0.070	0.136	0.225	0.336	0.477	.....
1.0	0.010	0.038	0.090	0.171	0.279	0.418	.....
				hb = 0.8			
0	0.190	0.285	0.388	0.505	0.639	0.805	.....
1.0	0.014	0.054	0.127	0.233	0.369	0.539	.....
				hb = 0.5			
0	0.237	0.376	0.528	0.705	.....	.....	.....
1.0	0.032	0.122	0.263	0.436	.....	.....	.....

evaluated, it will become apparent that this simple relation holds well within the range of practical interest for small sizes and even large sizes when slowly cooled.

III. Evaluation of Cooling Constants

In order to apply the broad relations of Tables I and II to spe-

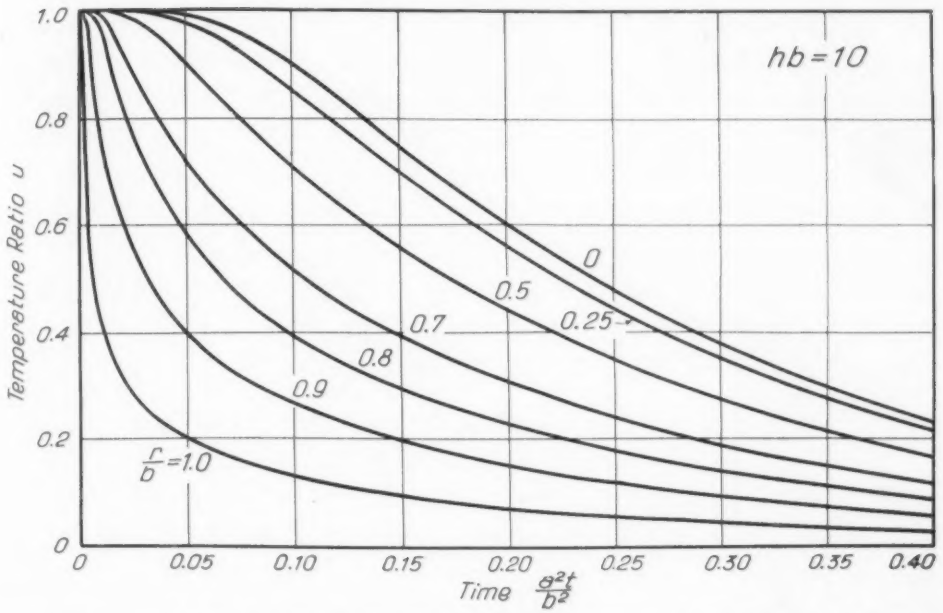

Fig. 1—Calculated Time-Temperature Cooling Curves at Several Points Between Center and Surface of Long Cylinders. These Curves are Representative at High Temperatures of a 1-inch Diameter Cylinder Quenched in Agitated Water.

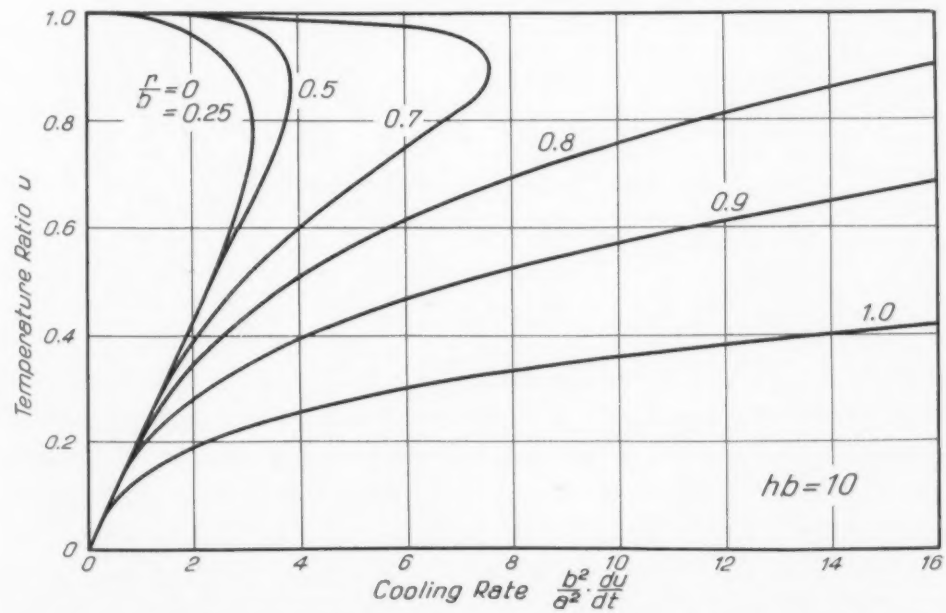

Fig. 2—Cooling Rates Calculated for the Same Conditions as Fig. 1 and Plotted Against Temperature at the Point and Instant at which Cooling Rate is Determined.

cific problems it is necessary to evaluate the diffusivity a^2 of ordinary steels and the quenching constant h for the more important quenching media. The evaluation of diffusivity is most important for, once

known, the quenching constant of a bath can be readily evaluated from the cooling time or rate at the center. Cooling at the center is determined relatively easily and considerable data are available for cylinders during quenching in several media.

A source of discouragement to the application of the equations of transient heat flow has been failure to recognize the fact that the

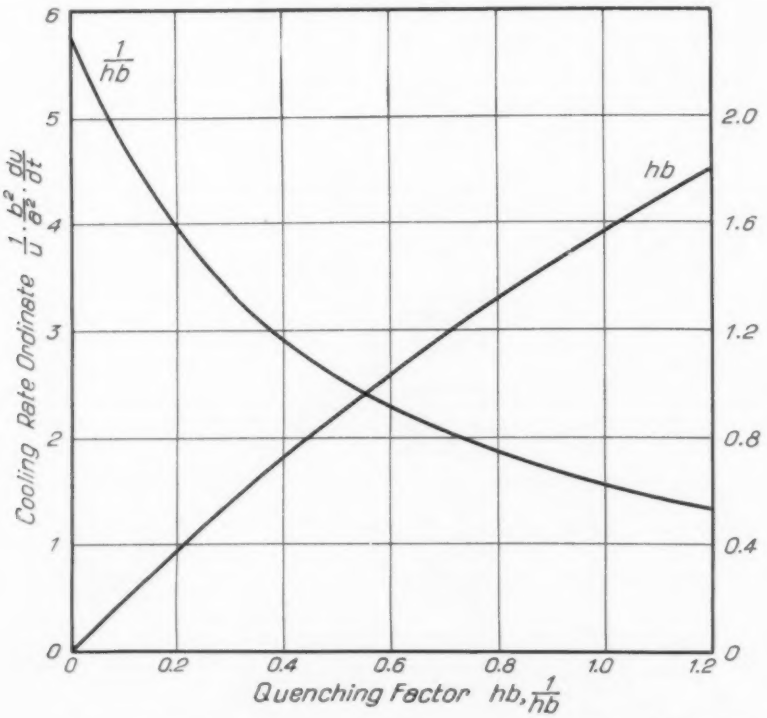

Fig. 3—General Relation Between Cooling Rate and Quenching Factor for Temperatures at which Cooling Rate at any Point within Cylinder is Proportional to Temperature at that Point.

diffusivity of steel above the critical range is greatly different from that below. Unfortunately little or no reliable data on this property of steel determined at high temperatures are available. If the diffusivity of austenite be assumed to be the same as that of pearlite, a calculated value of cooling rate is found which is much faster than the observed rate for that condition.

The diffusivity of austenite is much lower than that of pearlite, even at the same temperature, because the former constituent carries its carbon in solid solution. Carbon, and other elements as well, when in solid solution, in either alpha or gamma iron, lowers thermal conductivity greatly, but changes specific heat and density comparatively little. The thermal conductivity of a 1.0 per cent carbon,

1.3 per cent chromium pearlitic steel is 0.10[4] and that of the same steel in the martensitic condition is 0.066. The thermal conductivity of austenite is still lower than that of martensite. It changes little with temperature when lowered by elements in solid solution and the diffusivity changes still less. Cooling rates are most significant when steel is austenitic.

The foregoing observations on the change in diffusivity with constitution must be recognized in using the mathematical relations,

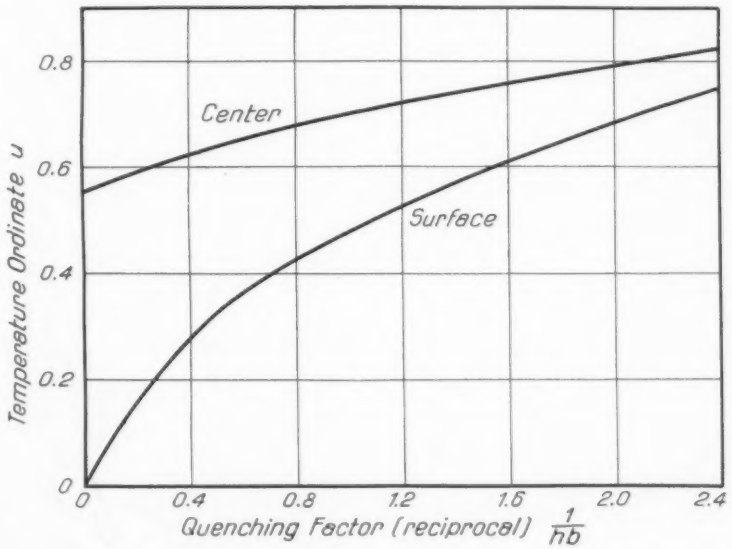

Fig. 4—Temperatures Below which Cooling Rate is Proportional to Temperature.

particularly when hardening is not complete, that is, pearlite is an end product. When hardening is complete, however, austenite transforms to martensite of nearly the same diffusivity at a low temperature with a comparatively small heat evolution so there is only a minor discontinuity in heat flow. However, the cooling rate has only secondary importance when the temperature is as low as that of the austenite-martensite transformation.

In view of the lack of information on diffusivity, an effort was made to evaluate this property. Approximate values may be obtained from the cooling rate at the center of large cylinders quenched rapidly by assuming $h = \infty$. It is only necessary to calculate the value of $\frac{b^2}{a^2} \cdot \frac{du}{dt}$ for $h = \infty$ and the temperature involved and substitute

[4]All units are in the Cgs system.

Table II

Calculated Relations Between Cooling Rate, Temperature, Size, Position and Cooling Constants for Long Cylinders so Cooled That Temperature Gradient at Surface is Proportional to Surface Temperature

$\frac{r}{b}$	Values of $\frac{b^2}{a^2} \cdot \frac{du}{dt}$ for U =						
	0.90	0.80	0.70	0.60	0.50	0.40	0.30
				hb = ∞			
0	3.38	3.78	3.68	3.33	2.83	2.29	1.73
0.5	5.05	5.05	4.44	3.67	2.93	2.30	1.73
.7	14	11.2	8.5	5.92	4.30	2.93	1.85
.8	38	24	16.9	11.9	7.4	4.54	2.58
.9	..	..	....	....	22	13.1	6.19
1.0	..	..	....	....	..	....	....
				hb = 10			
0	2.75	3.15	3.07	2.75	2.37	1.90	1.43
0.5	3.82	3.78	3.40	2.87	2.37	1.90	1.43
.7	7.60	6.75	5.30	4.00	2.90	2.10	1.43
.8	15.8	11.6	8.20	5.65	3.90	2.57	1.62
.9	36	27	16.8	11.4	7.1	4.2	2.25
1.0	..	..	....	....	31	14	6.0
				hb = 5			
0	2.40	2.67	2.57	2.33	1.98	1.58	1.18
0.5	3.12	3.08	2.75	2.38	1.98	1.58	1.18
.7	5.43	4.78	3.78	2.90	2.22	1.65	1.18
.8	8.7	7.17	5.25	3.75	2.63	1.82	1.25
.9	18.5	13.6	8.75	5.85	3.80	2.35	1.38
1.0	....	....	....	13	7.50	4.10	2.05
				hb = 3			
0	2.00	2.20	2.10	1.88	1.60	1.28	0.97
0.5	2.43	2.47	2.22	1.92	1.60	1.28	0.97
.7	4.00	3.40	2.69	2.12	1.63	1.28	0.97
.8	5.98	4.66	3.41	2.52	1.79	1.30	0.97
.9	11.5	7.8	5.0	3.32	2.20	1.47	0.97
1.0	....	17	9.9	5.45	3.20	1.85	1.08
				hb = 1.6			
0	1.54	1.62	1.51	1.33	1.11	0.88	0.66
0.7	2.54	2.06	1.68	1.37	1.11	0.88	0.66
0.9	5.5	3.45	2.31	1.61	1.19	0.88	0.66
1.0	...	5.7	3.50	1.98	1.29	0.91	0.66
				hb = 1.0			
0	1.19	1.20	1.10	0.95	0.79	0.63	0.47
0.7	1.68	1.37	1.13	0.95	0.79	0.63	0.47
0.9	3.02	1.83	1.29	1.00	0.79	0.63	0.47
1.0	5.0	2.47	1.49	1.06	0.81	0.63	0.47
				hb = 0.8			
0	1.03	1.02	0.92	0.79	0.66	0.53	....
1.0	3.6	1.76	1.11	0.83	0.66	0.53	....
				hb = 0.5			
0	0.74	0.70	0.62	0.53	0.44	....	....
1.0	1.60	0.84	0.63	0.53	0.44	....	....

it in the following equation with the observed values:

$$a^2 = \frac{b^2}{C} \cdot \frac{1}{(Ti\text{-}To)} \cdot \frac{dT}{dt}$$

where C is the calculated value of $\frac{b^2}{a^2} \cdot \frac{du}{dt}$. This gives appar-

ent values which are low, but approach close to the true value for severe quenches and large sizes provided hardening is complete.

Apparent values of diffusivity have been calculated as indicated and plotted in Figs. 5 and 6 against diameter of cylinder. The experimental data are taken from published results of French[5] and of Portevin and Garvin[6] and from some observations made by the author using an experimental method previously described.[7] Since the

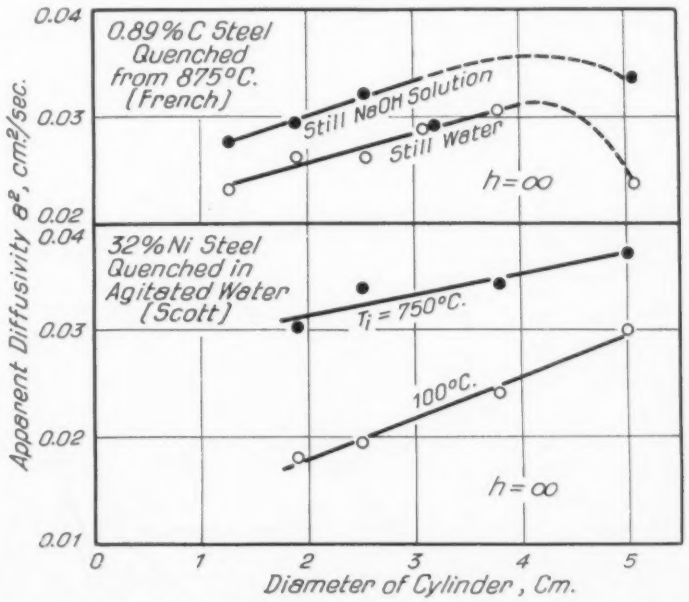

Fig. 5—Values of Diffusivity Estimated from Observed Cooling Rates at Center of Cylinders During Quenching Assuming Infinitely Rapid Surface Cooling.

curves drawn should approach asymptotically a constant value as diameter is increased, the diffusivity of 0.9 per cent carbon is at least 0.035 and that of 32 per cent nickel steel close to 0.040 at high temperatures according to Fig. 5. The correspondence between a 0.9 per cent carbon steel and a high nickel steel is demonstrated by Fig. 6 also. There the great difference in diffusivity between pearlite (steel quenched from 630 degrees Cent.) and austenite (same steel quenched from 760 degrees Cent.) is well illustrated. These observations, however, do not go to large enough diameters to give a reliable value of diffusivity.

[5]French, "The Quenching of Steels."

[6]Portevin and Garvin, *Journal*, Iron and Steel Institute, Vol. 99, 1919, p. 469.

[7]Scott, TRANSACTIONS, American Society for Steel Treating, Vol. 6, 1924, p. 13.

A more satisfactory means of determining diffusivity is to observe cooling at two widely separated points on a radius. Then only one particular value of h and a^2 will yield calculated curves which coincide with the experimental, hence the quenching constant is also determined by such observations. This method is inconvenient to

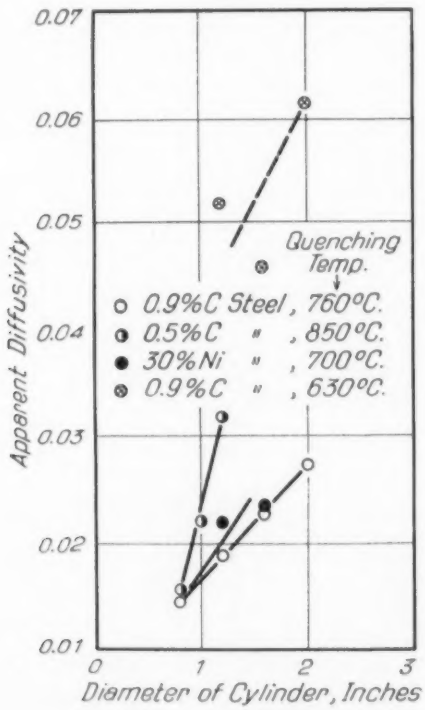

Fig. 6—Values of Diffusivity Estimated as in Fig. 5 from Observations of Portevin and Garvin on Steels Quenched in a Water Spray.

apply to steels which transform during quenching, but from the preceding paragraph we know that an austenitic nickel steel has practically the same diffusivity as a eutectoid carbon steel and therefore is representative of such a steel.

This method of determining diffusivity was applied to a 32 per cent nickel steel, the thermal properties of which near room temperature are:

Thermal conductivity	0.035
Specific heat	0.120
Density	8.131

Consequently its diffusivity is 0.034 square centimeters per second somewhat above room temperature.

As a test of the method, cooling curves were taken by the writer

at the center and 0.84 inch from the center of a 2-inch diameter cylinder during quenching in ice water from boiling water. The time-temperature observations for a quench with slow stirring are plotted in Fig. 7 and those for faster stirring in Fig. 8. The curves were calculated for the values of the constants given. It may be noted that the observed and calculated values are in excellent accord throughout the whole range. This agreement provides substantial

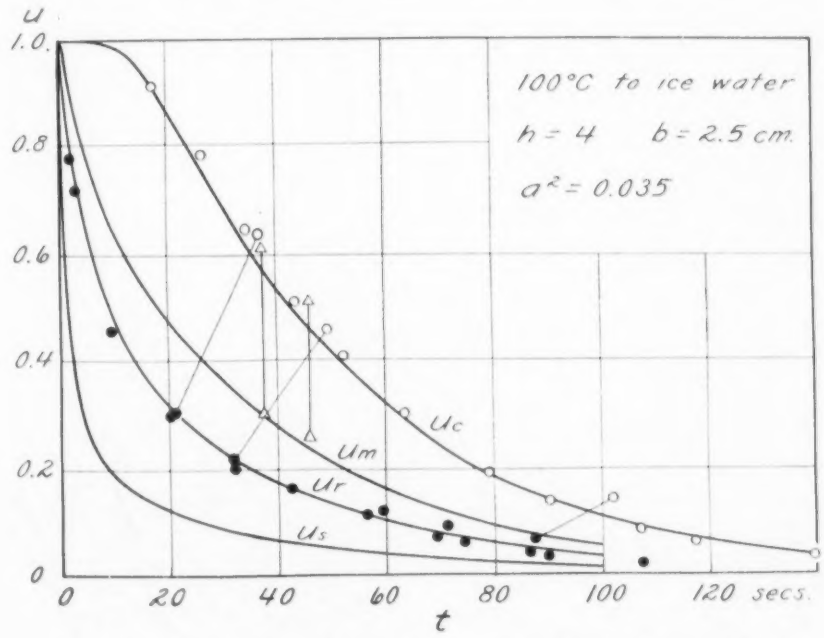

Fig. 7—Cooling Times for 32 Per Cent Nickel Steel Cylinder 2 Inches in Diameter Observed During Quenching in Water at 0 from 100 Degrees Cent. and Compared with Calculated Curves. Uc is Temperature at Center, Um is Mean Temperature, Ur Temperature 0.84 inch from Center and Us Surface Temperature.

justification for the initial assumption that the gradient at the surface is proportional to the surface temperature over short temperature ranges, and engenders confidence in the method.

Another related method of doing the same thing with only one thermocouple is to determine the center and mean temperature at the same instant during a quench. This is done by withdrawing the specimen as a certain center temperature is reached and cooling in air or silocel. From the cooling curve in air the mean temperature at time of withdrawal is estimated. Only one value of h and a^2 will yield by calculation that center and mean temperature. Some observed values of center and mean temperature (Um) are plotted and agree well with the calculated values. The surface temperature (Us)

was also calculated for the values of the constants given in the figures and though obviously an extrapolation of the observed data, cannot be far removed from actuality.

The different experiments and methods agree in requiring a diffusivity value of 0.035 for this steel over the temperature range 0 to 100 degrees Cent. This is within the limits with which its diffusiv-

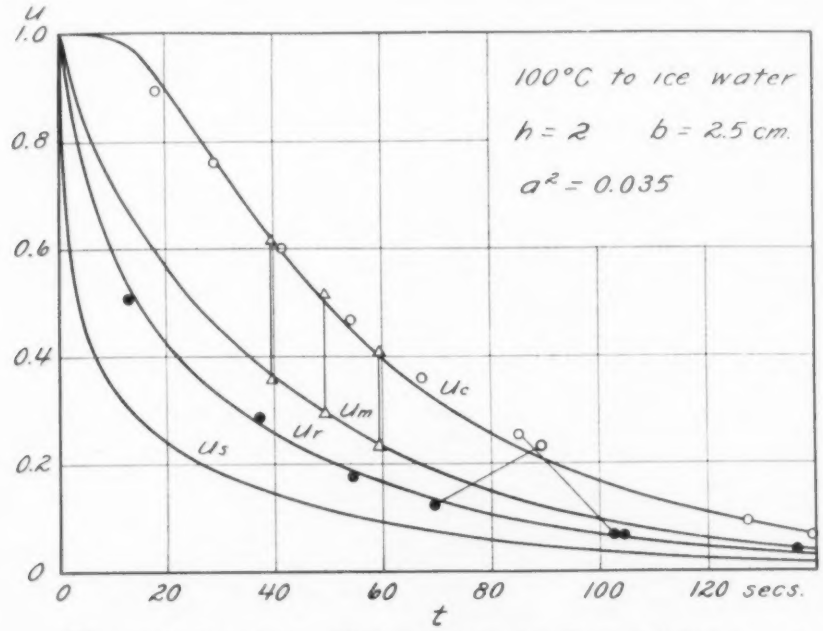

Fig. 8—Cooling Curves Obtained Under the Same Conditions as in Fig. 7 Except that Stirring was Less Vigorous.

ity was determined directly. One may use the method with confidence for the estimation of diffusivity at elevated temperatures.

Fig. 9 gives the cooling curves of the same cylinder during quenching in water with stirring from 750 degrees Cent. In this case the curves, which were calculated for values of a^2 and h that correspond well at high temperatures, do not agree with the observed values at low temperatures. A lower diffusivity evidently contributes to the slower cooling at low temperatures, but the drop in h is the more important factor.

The value of diffusivity for the 32 per cent nickel steel at high temperatures is evidently 0.045. Cooling curves for the center of a 1.0 per cent carbon, 1.3 chromium steel 1 inch diameter were found to be identical with that for the same size 32 per cent nickel steel at high temperatures with the same water quench so their diffusivities must be nearly identical. As a result of these observations a dif-

fusivity value of 0.040 was taken as representing medium and high carbon steels of moderate alloy content when in the austenitic condition. Though this value may not be the best for the purpose, it certainly is not sufficiently in error to detract seriously from the con-

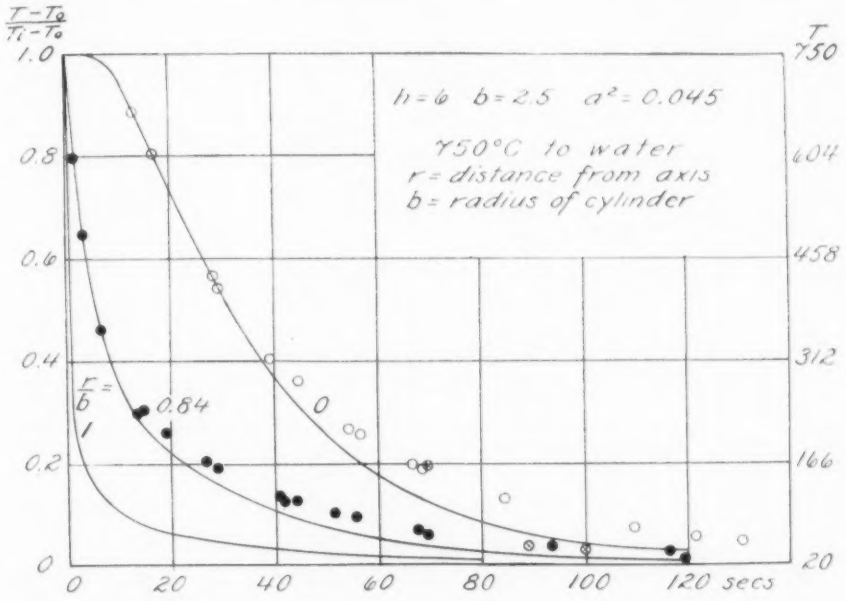

Fig. 9—Observed Cooling Times at Center and 0.84 Inch from Center of a 2-inch Diameter Cylinder of 32 Per Cent Nickel Steel Taken During Quenching in Water with Agitation from 750 Degrees Cent. The Curves were Calculated for the Values of the Cooling Constants Noted.

clusions drawn on the basis of it. If future work requires a modification, a correction can easily be applied to the relations derived in the following sections.

IV. Variation of Cooling Rate with Diameter

Complete hardening of steels is essential to obtain identical mechanical properties throughout a section when the required properties are so high that they can be obtained only by quenching. The cooling rate at the center of a piece where it is slowest must therefore exceed the critical cooling rate of the steel used if the condition of complete hardening is to be fulfilled. Critical cooling rate is here used to express the minimum rate that will produce a completely martensitic structure.

Available data on the critical cooling rates of steels, particularly alloy steels, are meagre. Nevertheless considerable information exists from which approximate values for important steels can be ob-

tained. For example, Jones[8] gives hardness observations on nickel steels cooled at different rates from which the critical cooling rate of the familiar 0.30 per cent carbon, 0.8 per cent manganese, 3.5 per cent nickel steel is found to be about 32 degrees Cent. per second. According to the data of French[9] the critical cooling rate of a carbon steel of the same carbon and manganese content is around 500 degrees Cent. per second. Consequently, if the relations between cooling rate at the centers as related to the diameter of cylinders were known for quenching in standard media, one could estimate at once the maximum size of these steels, which can be fully hardened in the quenches evaluated.

To carry out this project one must adopt some convention regarding the temperature at which the cooling rate shall be measured. The pioneer work of Bain[10] on rates of reaction during quenching shows that in carbon steels the rate of reaction is a maximum at about 550 degrees Cent. Consequently the rate of cooling has major importance at this temperature and should be measured there, at least when martensite is an expected end product. The cooling rate may be considerably lower than the critical rate at either higher or lower temperatures without initiating the formation of a pearlitic constituent providing it exceeds the critical rate at the temperature of maximum reaction rate and cooling is continuous. The temperature range of maximum reaction rates is rather broad and probably occurs at practically the same temperature for moderately alloyed steels as for carbon steels.

The major obstacle to the proposal set forth is that quenching has not been standardized in any way. Water quenching gives a wide range of cooling rates depending on temperature of the water and degree of agitation. The most reproducible water quench, and probably the fastest quench attainable as well, is that provided by the submerged water spray by means of which high pressure jets are made to impinge on all surfaces of the submerged piece. This quench provides a very useful reference point, but unfortunately no information is available on the cooling rates obtained with it. The situation with oil quenching is even less satisfactory for the compositions of quenching oils are not well defined and their character-

[8]J. A. Jones, *Journal*, Iron and Steel Institute, Vol. 117, 1928, p. 295.

[9]H. J. French, "The Quenching of Steels."

[10]E. C. Bain, TRANSACTIONS, American Society for Steel Treating, Vol. 20, 1932, p. 385.

istics change with use. Nevertheless it is worth while to review the information available on the effects of quenching media for it will give a fair idea of the relations between different types of media and their relative effectiveness.

French has made the most complete study of size effects in cylinders. His observations were made on a eutectoid carbon steel and are plotted in Fig. 10. Since the A_1 transformation starts in the larger sizes above 550 degrees Cent., the cooling rate was necessarily taken at a higher temperature, 720 degrees Cent. The curves drawn were calculated for that temperature, $a^2 = 0.040$ and that value of h which gave best correspondence with the observations. From Fig. 2 it may be seen that there is little change in cooling rate at the center between this temperature, $u = 0.82$, and 550 degrees Cent., $u = 0.62$. The curves are representative of cooling rates at the lower temperature.

The two lower curves of Fig. 10 represent very well the observed cooling rates throughout the whole range of sizes, ½ to 2 inches diameter. Consequently they may be used with some confidence to extrapolate to larger or smaller sizes. It should be recognized, however, that, since the larger sizes require longer times of heating, the scale formed is heavier and acts to retard cooling. A lower value of h than indicated should therefore be used to represent cooling unless a controlled atmosphere is used in the heat treating furnace to prevent scale formation.

Observations of center cooling rates at 550 degrees Cent. are plotted in Fig. 11 against diameter of cylinder. Again the experimental data line up well with the calculated curves. Portevin and Garvin's water spray is not so effective as still water, probably because of low pressure and incomplete covering. The writer's observations of cooling in water with brisk agitation taken from the time-temperature curves of Fig. 12 are certainly closer to a submerged spray quench, than is Portevin and Garvin's spray quench. The curve for agitated oil is probably representative of ordinary practice when a fast oil is used and there is little scale on the steel.

Air-cooling is often used to enhance the properties of steel. Fig. 13 gives observed air-cooling rates plotted against diameter of cylinder. Here also the shape of the calculated curves matches well that of the observed values though there is a slight tendency for the observed values to be lower at large sizes, probably because of heavier scaling. The upper curve was determined by observations on carbon steels, hence the temperatures, 700 to 720 degrees Cent., at

which the cooling rates were taken. The corresponding value of h should be used for steels which are pearlitic as cooled.

With cooling as slow as that in air, the cooling rate becames proportional to the temperature shortly after the start of the quench. Hence, the cooling rate at 550 degrees Cent. is less than that at 700 degrees Cent. Also the value of h drops considerably so the total

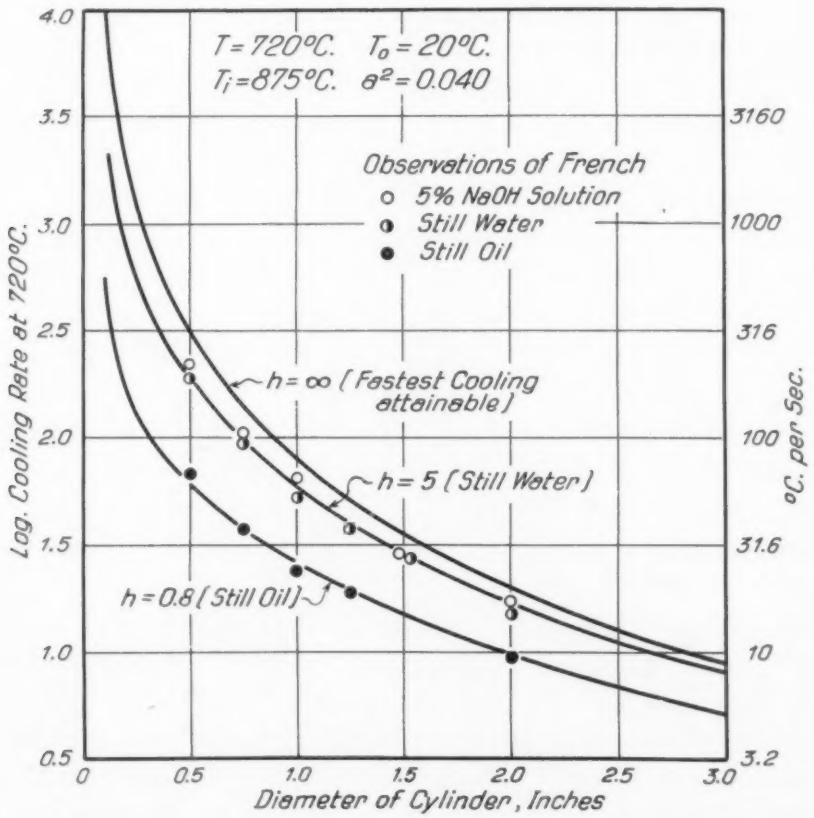

Fig. 10—Calculated Variation in Cooling Rate at Center with Diameter of Cylinder. The Individual Values Plotted were Observed by French on 0.89 Per Cent Carbon Steel Quenched as Indicated.

change in rate is quite large as shown by the lower curve of Fig. 13 which gives cooling rates at 550 degrees Cent. This curve is calculated for a somewhat lower value of h than observed at the same temperature with 32 per cent nickel steel so that it represents more nearly low alloy content steels which scale more freely than the austenitic nickel steel. Information taken from the curve for cooling rate at 550 degrees Cent. should be applied only to steels cooled at rates near or above their critical cooling rate. The upper curve may

be taken also as indicative of cooling rates at 550 degrees Cent. during cooling over a fan.

Table III

Cooling Rates Obtained at Center of Cylinders of Three Different Diameters for Several Quenches. Values of h Calculated for $a^2 = 0.040$

Quenching Medium	Temperature at Center Degrees Cent.	h	Cooling Rate in Degrees Cent. Per Second for Diameter of 1"	2"	3"
Instantaneous surface cooling	720	∞	79	20	8.9
	550	∞	69	17	7.6
Agitated water at 10-20 degrees Cent.	550	8	56	15	7.4
Still water at 10-20 degrees Cent.	720	5	60	17	7.9
Agitated water at 0 degrees Cent.	50	3	46	14	6.6
Agitated oil	550	1.2	27	10	5.2
Still oil	720	0.8	26	9.8	5.1
Still air	720	0.040	1.8	0.88	0.57
Air stream	550	0.055	1.8	0.88	0.57
Still air	550	0.025	0.85	0.42	0.27

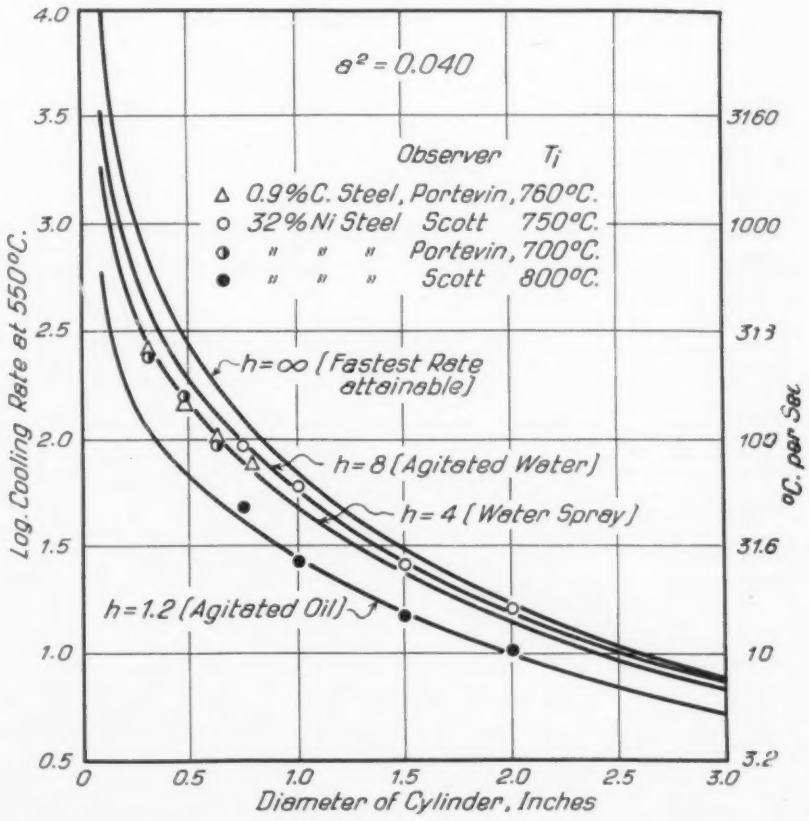

Fig. 11—Calculated Variation in Cooling Rate at Center with Diameter of Cylinder Compared with Values Observed for Several Sizes and Quenching Media.

The data presented on effects of diameter served to establish approximate values of h for several important quenching conditions.

These values are tabulated in Table III together with cooling rates of several diameters. Here we see that the large difference between the cooling rates for oil and water at small diameters, is not reflected in correspondingly large differences in cooling rates at large diameters. In fact the difference at small diameters is not great if expressed as the increment in diameter required to produce the same

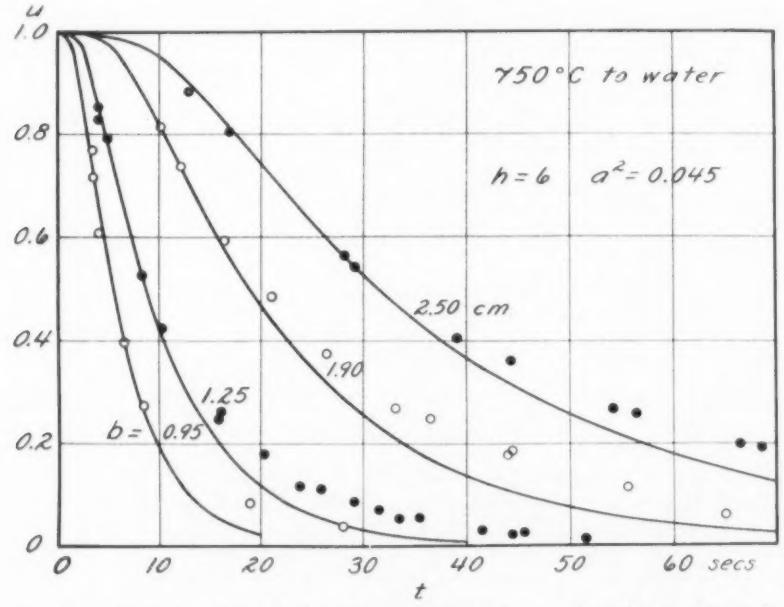

Fig. 12—Observed and Calculated Cooling Curves for Center of 32 Per Cent Nickel Steel Cylinders During Quenching in Water from 750 Degrees Cent. with Agitation.

rate with a water quench as obtained with an oil quench of a 1 inch diameter cylinder. Thus comparing quenches with agitation, Fig. 11, a cylinder 1.5 inches diameter will cool as fast in water as a 1.0 inch diameter cylinder will in oil. The rates for cooling in still air, however, are of very much smaller magnitude. A cylinder 0.1 inch diameter is the largest that will cool in air as fast as a 2.0 inch cylinder quenched in agitated oil. Evidently the critical cooling rate of a steel must be very low; perhaps less than 1.0 degree Cent. per second, before it can be classified as air-hardening.

V. Ultimate Limits of Cooling Rates

Much effort has been expended in the development of quenching media with the object of increasing the cooling rates obtainable therefrom over those obtained from conventional media. Mathematical relations such as those given here provide means for ascertaining how

far this type of improvement can go, a problem beyond the scope of purely experimental attack. The maximum rates of cooling physically attainable can be readily calculated and are as reliable as is our evaluation of cooling constants.

The fastest cooling rate attainable at the center of a cylinder of a given diffusivity (for a quenching range, Ti-To, of about 800 degrees Cent.) when the center is at 550 degrees Cent. is:

$$\frac{dT}{dt} = 2820 \frac{a^2}{b^2} \text{ degrees Cent. per second}$$

Assuming $a^2 = 0.040$, the rate in terms of the diameter is:

$$\frac{dT}{dt} = \frac{70}{D^2} \text{ degrees Cent. per second}$$

where D is diameter in inches.

The top curve of Fig. 11 was calculated from this relation. According to this figure an agitated water quench approaches very closely to giving the fastest rate possible at the center. Of course this relation would be changed if another value of diffusivity were used, but it is not conceivable that the value used is enough different from that of ordinary steels to affect materially the validity of the foregoing conclusion.

Two advantages of quenching speeds approaching closely to the highest attainable may be mentioned. One is complete hardening in larger sizes than is possible with a less active quench. That provides a saving in alloy content when complete hardening is required. It is quite evident from Fig. 11 however, that the possible gain in this direction is rather insignificant. Also it is offset by the greater distortion to be expected with increased quenching activity.

The major application for quenches of great activity is to shallow hardening steels, that is, plain carbon steels. Of particular interest is the widely used 1.0 per cent carbon tool steel which has been observed to harden to a depth of 0.17 inch in 1-inch rounds quenched in a submerged water spray. Seldom is so great a depth of hardening actually required by service conditions. A thin shell, if continuous, is usually preferable. If however, the quenching capacity of the bath be lowered to give a much thinner shell, trouble will be experienced with continuity of the shell because of reduction in the cooling rate gradient near the surface.

The advantage of applying a coolant possessing exceptional activity to shallow hardening steels is illustrated by Fig. 15 where cooling rate is plotted against reciprocal h so as to show the variation in cooling rate up to infinite values of h. The origin of this figure corresponds to instantaneous surface cooling, $h = \infty$, the fastest conceivable with the chosen value of diffusivity. It may be seen that on diminishing the activity of the quench (increasing 1/h) the cool-

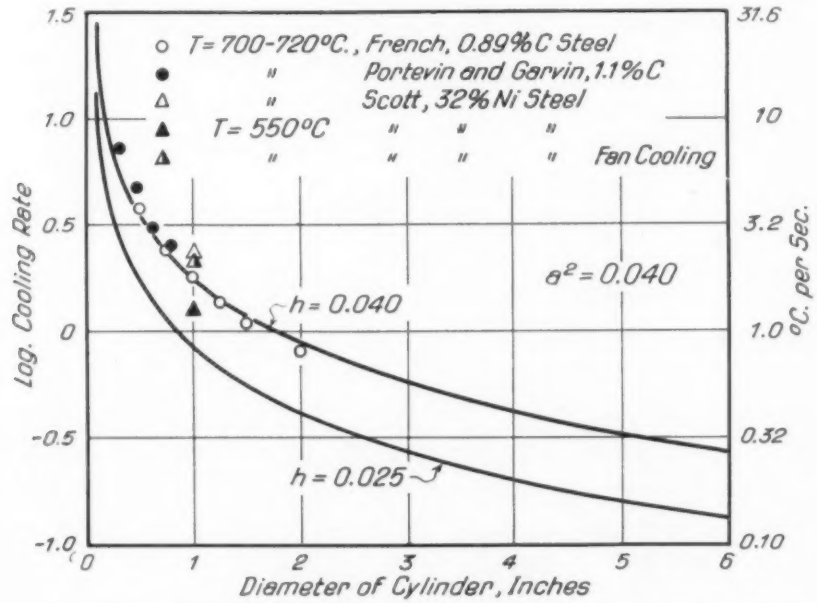

Fig. 13—Calculated Variation in Cooling Rate at Center with Cylinder Diameter for Air-cooling. The Individual Values Plotted were Observed under the Conditions Noted.

ing rate near the surface drops very rapidly with respect to that more remote from the surface. Thus with mild water quenches there is less margin of excess cooling rate to insure hardening in unfavorably situated regions of complicated shapes than there would be with more drastic ones. This is shown clearly by Fig. 16 also where cooling rate is plotted against distance from the surface.

The highly desirable feature of an exceptionally active quench, excess cooling rate near the surface, is offset by deeper penetration of hardening. This disadvantage however, may be overcome by the use of a steel that hardens less deeply than the one previously mentioned. Steels are available into which hardening penetrates only to 0.10 inch from the surface of a 1-inch round with the submerged water spray quench. The most important advantage of the intense quenches appears to be to make practicable the use of such steels. If

the hardened shell is sufficiently thin, volume changes which are partially responsible for distortion are minimized and this tends to compensate for the adverse effects of faster quenching. Moreover, the shallow hardening carbon tool steels are characteristically fine

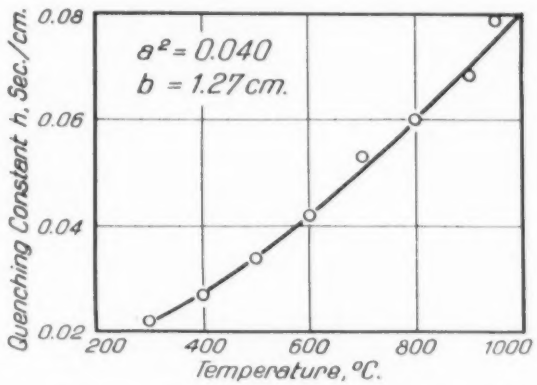

Fig. 14—Change in Magnitude of Quenching Constant with Surface Temperature During Cooling in Still Air of 1-inch Diameter Cylinder of 32 Per Cent Nickel Steel.

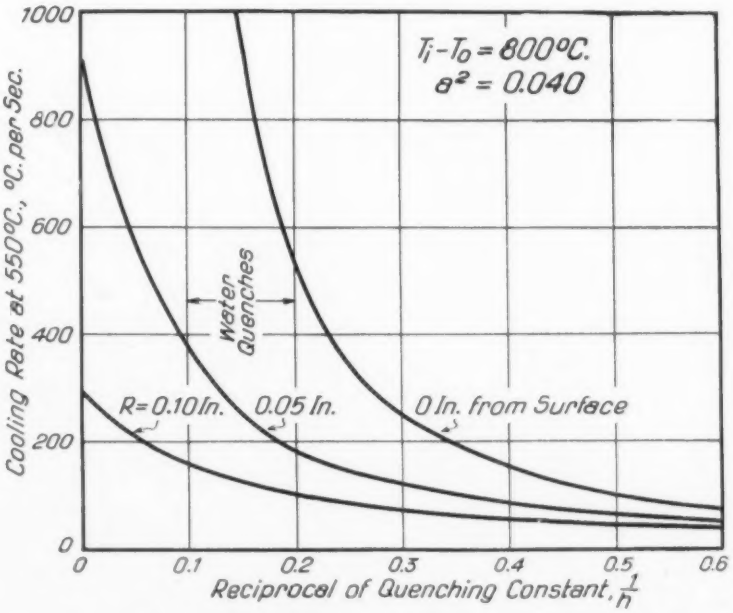

Fig. 15—Calculated Variation of Cooling Rate Near Surface of a 1-inch Diameter Steel Cylinder with Activity of Quench.

grained and this property is of considerable value in certain respects.

The manner in which penetration of hardening varies with size of cylinder is also pertinent to the present subject. Cooling rates were calculated for points near the surface with a high value of h

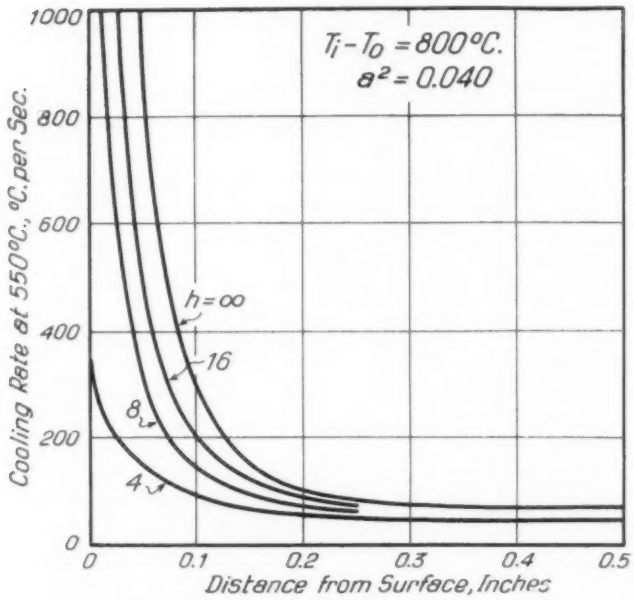

Fig. 16—Variation in Cooling Rate with Distance from Surface Calculated for 1-inch Diameter Steel Bar.

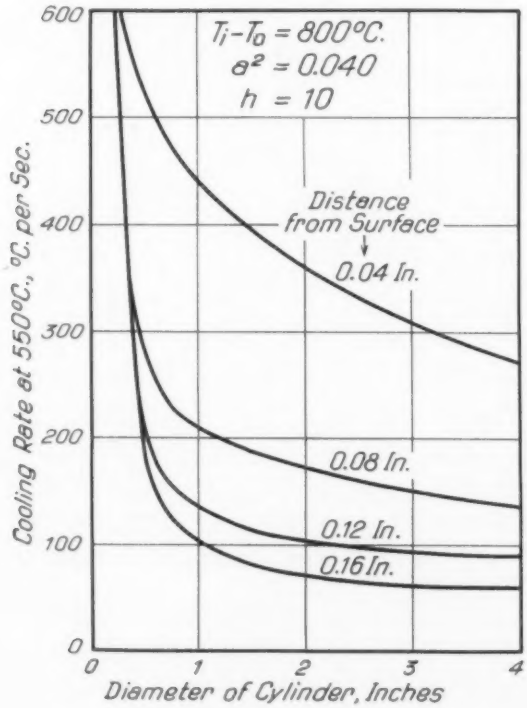

Fig. 17—Variation in Cooling Rate Near Surface with Diameter of Cylinder Calculated for a Well Agitated Water Quench.

and plotted against diameter in Fig. 17. The curves have flattened out considerably by the time the size has increased beyond 2 inches diameter, indicating little diminution in penetration of hardening with further increase in size. Calculating similar curves for several other positions, one may plot the equivalent of penetration of hardening, that is, the position of the elements cooling at a particular critical

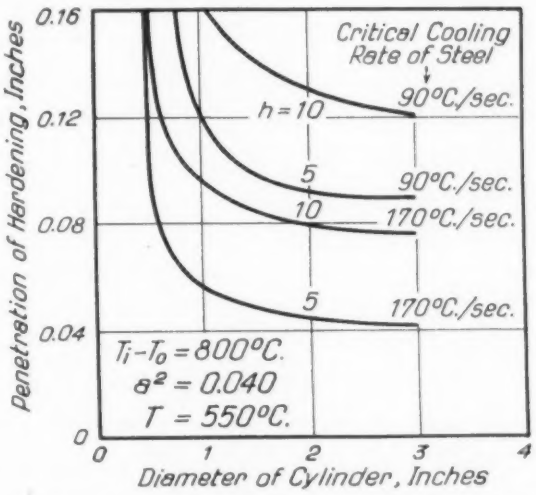

Fig. 18—Estimated Penetration of Hardening (Depth of Complete Martensitization) in Carbon Steels of Low and High Critical Cooling Rates Plotted Against Cylinder Diameter. h = 5 Represents a Mild Water Quench and h = 10 a Well Agitated Water Quench.

cooling rate, against cylinder diameter as in Fig. 18. The upper curves represent a steel which hardens to a depth of 0.17 inch in a 1-inch round with a submerged water quench and the lower curves a steel which hardens to a depth of 0.10 inch. These curves are indicative of maximum and minimum penetration values for 1 per cent carbon steels.

The questions so far discussed serve well to illustrate the type of problems that can be solved by the means employed here. Many others may be handled in a similar manner but are beyond the scope of this paper. Attention has been given to several related problems which may be reported at a later date.

VI. Summary and Conclusions

The equations of transient heat flow in a long cylinder derived on the assumption that the temperature gradient at the surface is proportional to the surface temperature represent very well experi-

mental cooling curves observed during quenching over moderate temperature ranges. The temperature ranges of correspondence are sufficiently long to permit important deductions regarding the effects of the major variables of quenching as it is usually practiced.

Of the two constants required for solution of quenching problems, one, the diffusivity, is a characteristic of the steel and the other, the quenching factor, is a characteristic of the bath for steels of the same thermal conductivity. Both constants were evaluated approximately for common steels and several quenching media. The diffusivity was estimated for steels in the austenitic condition because the cooling rate while the steel is in that state determines the end products of a quench.

The calculations necessary for the application of the equations of transient temperature change in a long cylinder were made and tabulated in a condensed form from which the effects of any one of nine factors concerned can be easily deduced. The variation of cooling rate at a significant temperature with several of the important variables was studied in detail and compared with experimental results so far as possible. These studies led to the conclusions:

(1) Cooling rate distribution can be determined by the method used under conditions not amenable to purely experimental attack.

(2) The cooling rate at the center of a long cylinder is indicative of the maximum size that can be fully hardened and can be estimated for water, oil or air quenching from its diameter with fair assurance.

(3) The cooling rates at the center of cylinders quenched in water or oil do not vary much from the maximum value over a considerable temperature range within which the rate of the Ar_1 reaction in the steel reaches a maximum.

(4) During the quenching of larger cylinders in air or of very small ones in oil or water, the maximum cooling rate is reached shortly after beginning the quench and cooling thereafter is expressed by very simple relations.

(5) As diameter is increased the advantage of water over oil quenching in producing faster cooling at the center tends to diminish provided other factors do not change excessively.

(6) A well agitated water quench approaches close to the fastest physically attainable as judged by the cooling rate at the center.

(7) The chief advantage of exceptional quenching power is to insure uniform shallow hardening in fine-grained steels.

Appendix

Equations for Cooling of Long Cylinders When Temperature Gradient at Surface is Proportional to the Surface Temperature

Using the symbols for the major variables of quenching defined in the text, the cooling at points remote from the ends of a long cylinder is given by:

$$u = \Sigma A_n \cdot e^{-a^2\mu_n^2 t} \cdot J_o(\mu_n r) \quad \ldots\ldots (1)$$

where Σ indicates summation of all terms of the series from n = 1 to n = ∞, n being the positive integers.

e is the base of the Naperian logarithms. Five terms were used in the calculations and are sufficient to determine temperatures accurately except for very small values of $a^2\mu_n^2 t$.

The value of μ_n is determined by the relation:

$$hb \cdot J_o(\mu_n b) = (\mu_n b) \cdot J_1(\mu_n b) \quad \ldots\ldots (2)$$

where $J_o(\mu_n b)$ and $J_1(\mu_n b)$ are Bessel's functions of the zeroth and first orders respectively. Values of these functions are given in the Smithsonian Tables and certain mathematical texts.

A_n is a constant for a particular value of hb given for each term in the series by:

$$A_n = \frac{2hb}{(h^2b^2 + \mu_n^2 b^2) \cdot J_o(\mu_n b)} \quad \ldots\ldots (3)$$

Cooling rates may be found by differentiating U with respect to t:

$$-\frac{du}{dt} = \Sigma a^2\mu_n^2 A_n \cdot e^{-a^2\mu_n^2 t} \cdot J_o(\mu_n r) \quad \ldots\ldots (4)$$

and the mean temperature, Um, by an integration yielding:

$$u_m = 2\Sigma \frac{J_1(\mu_n b)}{(\mu_n b)} \cdot A_n \cdot e^{-a^2\mu_n^2 t} \quad \ldots\ldots (5)$$

In the later stages of a quench indicated by Fig. 4, cooling times and rates are given by the first term of the series, thus simplifying the respective equations to:

$$u = A_1 \cdot e^{-a^2\mu_1^2 t} \cdot J_o(\mu_1 r) \quad \ldots\ldots (6)$$

$$\frac{-du}{dt} = a^2\mu_1^2 u \quad \ldots\ldots\ldots\

The rate of cooling of a cylinder immersed in a quenching bath would be the greatest possible when the temperature of the liquid layer in contact with the steel remains strictly constant at its initial value; in other words, when the steel surface can be regarded as coming instantaneously to the temperature of the bath and remaining there; under these conditions the rate of cooling depends only on the heat diffusivity of the steel. The maximum rate, calculated on this basis, for 720 degrees Cent., in Fig. 10 is comparatively little greater than the actual rate observed on specimens quenched in still water or 5 per cent NaOH solution. Such quenching baths, therefore, appear to be measurably close to the ideal, insofar as rapidity of quenching at 720 degrees Cent. is concerned. It would be interesting to make a similar comparison at 550 degrees Cent., the temperature region of maximum transformation rate in steel.

On pages 74 and 75 the author points out that there is a great difference between the thermal diffusivity above and below the critical range. Since no reference is given in the paper, it would be interesting to know whether the data on which this conclusion is based were obtained by Mr. Scott or were taken from the literature.

In the summary (page 92) under (7) the author points out the importance of a rapid quench to insure uniform hardening in fine-grained steel. Although this statement is correct, it does not seem to follow from the deductions given in the paper, since it depends on the specific physical-chemical properties of the steel.

A. L. FEILD:[2] I would like to ask Mr. Scott one question, and that is how he determined the value h. It would seem to be a function of the surface temperature. I would like to know whether he assumed it to be some fraction of the quenching medium temperature.

Author's Closure

In response to Mr. Feild's question, it should be stated again that the quenching constant h is a function of the surface temperature over a long temperature range. It must, of course, be assumed to be a constant in calculating cooling rates and the comparisons between observed and calculated cooling curves show clearly that this assumption is justified for certain temperature ranges and quenching media of particular interest. Perhaps it will clear up the confusion regarding the significance of this constant to say that it is the ratio of the temperature gradient at the surface to the surface temperature.

With regard to the evaluation of h for steels, the method used has been outlined in principle. Actually in the most important case of water quenching, the method used was to plot to the same scale observed cooling curves at the center and near the surface together with theoretical curves computed for assumed values of h and a^2. Of all the possible values of these constants, only one pair will give theoretical curves which match the observed curves at both positions. The values producing a match are taken as representative of the quench and specimen over the temperature range of good correspondence between the observed and theoretical curves. Once the diffusivity of the test specimen is known, the value of h for any quenching medium and surface tem-

[2]President, Alloy Research Corp., Baltimore.

perature can be calculated from the cooling rate at a single position and an appropriate temperature.

The writer appreciates greatly the careful attention and study Dr. Heindlhofer has given to this paper and his elaboration of certain points which were given only scanty consideration in the interests of space conservation. He very properly makes the point that the rate of heat emission or abstraction during quenching varies considerably with surface temperature over the long temperature range of quenching. This is particularly true for quenching in oil and air. Since the value of the heat abstraction coefficient falls with surface temperature during cooling in those media and the temperature difference between center and surface increases with size, it follows that the value used for calculating cooling rates at a particular center temperature should be lower the larger the cylinder. This fact should, of course, be recognized in applying the derived cooling rate relations, though it is doubtful that such refinement is really in order until the diffusivity of common steels above the critical range is more accurately known.

Dr. Heindlhofer admits the propriety of calculating cooling rates near the center, but objects to extending the application to points near the surface. The issue now concerns water quenching only and more particularly quenching in agitated water. It is a well established fact that the heat abstraction coefficient is very low during the first stage of quenching in still water and his statement is probably based on such cooling observations. This stage, however, is eliminated by agitation, so the heat abstraction coefficient has a high and probably fairly steady value until the surface temperature reaches the boiling point of water. Confirmatory experimental evidence of this is afforded by Fig. 9. The temperatures observed near the surface during cooling fall on the curve calculated for an assumed constant rate of heat abstraction over a wide range of temperatures, 600 to 200 degrees Cent., so the change in the cooling coefficient with surface temperatures cannot be of important magnitude.

Evidence that the thermal diffusivity of a steel is greater at temperatures below the critical range than above is given by Portevin and Garvin and reproduced in Fig. 6. Also, the writer has observed a cooling rate at the center of a 1-inch diameter 1.0 per cent carbon, 1.4 per cent chromium steel after cooling through 0.60 of the temperature range during quenching in agitated water from above and below the critical range. In the first case the rate was 29 degrees Cent. per second and in the second 43. This indicates a diffusivity 50 per cent greater in the pearlitic condition than in the austenitic. Furthermore, he has found a thermal conductivity in an austenitic 1.34 per cent carbon, 0.89 per cent manganese steel at room temperature of 0.042 calories per centimeter per second per degree Cent. and of 0.100 in the pearlitic condition.

Dr. Heindlhofer points out an oversight in the last conclusion which should read: "The chief advantage of exceptional quenching power is to insure uniform surface hardening in fine grained carbon steels." The term carbon steels, of course, infers a low manganese content as well as a low content of other elements which lower the critical cooling rate.